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DECOMPOSITION OF HEPTANE AND OCTANE AT HIGH TEMPERATURES.

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The changes produced in organic compounds by destructive distillation, have not only been for many years a fruitful subject of scientific research, but have also opened up a great field of industrial chemistry. So numerous and complex are the resulting reactions that in many cases it is difficult to decide which really are the most valuable products obtained. Substances long treated as worthless by-products of these reactions are often found later to be most valuable. It was many years before coal tar was recognized as a valuable product in the manufacture of illuminating gas, but so many valuable substances have been made from it in the last two centuries that the gas might now be said to be a by-product of the tar. It is interesting to note in this connection that the first English patent concerning the dry distillation of coal, which was granted in 1681, had to do, not with the gas, but with the pitch and tar:—"A newe way of makeing pitch and tarre out of pit coale, never before found out or used by any other."

Of all the numerous by-products arising from such treatment of organic compounds upon a commercial scale, there are perhaps none of which so little is known as those which result from the manufacture of "Pintsch" gas from petroleum. The similarly formed decomposition-products of wood, shale, turf, peat, and bituminous coal have all received considerable attention, especially those of coal. In general, it may be said that the tars resulting from the destructive distillation of turf, of brown coal, and of bituminous shale consist mainly of aliphatic hydrocarbons, that from wood of phenols and their derivatives, that from bituminous coal of aromatic hydrocarbons. While these may be taken as distinguishing features of these various substances, secondary reactions greatly complicate the relations. The same elementary material by different treatment gives different results. Thus, by the action of relatively low heat upon coal we obtain a preponderance of hydrocarbons belonging to the paraffin, olefin, and acetylene groups, while, under the influence of a higher heat, the former decrease and the aromatic hydrocarbons increase.

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There have been many theories proposed to account for the change of hydrocarbons at high temperatures. That advanced by Berthelot in 1866[1] has long been accepted as the most plausible. In brief, his theory is that hydrocarbons do not decompose into carbon and hydrogen under the action of heat, but form higher and more complex molecules, this change taking place continually with increasing temperature. To quote his words: "Pure carbon is in some sense a limiting state and one which can scarcely be attained under the influence of the highest temperature we can produce." He divided pyrogenic reactions into two classes:

I. "Condensation moléculaire," or the direct combination of molecules with hydrogen or with each other.

II. "Décomposition inverse," or the breaking up of the hydrocarbon into a lower molecule and free hydrogen.

He maintained that a certain "equilibrium" exists between these two classes of reactions, which depends upon the temperature and upon the nature of the bodies acted upon, and that these two oppositely directed reactions take place simultaneously and mutually limit each other. According to his theory, the decomposition of methane would be explained by the following reactions:

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[1] Ann. Chim. Phys. [4], 9, 460.

$$\begin{aligned} 2CH_4 &= C_2H_4 + 2H_2, \\ 2CH_4 &= C_2H_2 + 3H_2, \\ C_2H_4 &= C_2H_2 + H_2, \\ C_2H_2 + H_2 &= C_2H_4, \\ C_2H_4 + H_2 &= C_2H_6, \\ 2C_2H_6 &= 2CH_4 + C_2H_2 + H_2, \text{ etc.} \end{aligned}$$

He explained the formation of aromatic hydrocarbons by the polymerization of acetylene:

$$3C_2H_2 = C_6H_6, \text{ etc.}$$

Jacobsen,[1] after investigating the subject, came to similar conclusions. To explain the formation of aromatic hydrocarbons from acetylene and allylene he proposed the following equations:

$$\begin{aligned} 3C_2H_2 &= C_6H_6, \text{ benzol,} \\ 2C_2H_2 + C_3H_4 &= C_7H_8, \text{ toluol,} \\ C_2H_2 + 3C_3H_4 &= C_8H_{10}, \text{ xylol,} \\ 3C_3H_4 &= C_9H_{12}, \text{ mesitylene.} \end{aligned}$$

Jacobsen did not believe that hydrogen was liberated by these reactions, but Anschütz[2] points out that, according to Jacobsen's theory, other hydrocarbons commonly occurring in such decomposition-products can be explained only by assuming that hydrogen is split off. Thus:

$$\begin{aligned} 5C_2H_2 &= C_{10}H_8, \text{ naphthalene, } + H_2, \\ \text{or} \begin{cases} C_{10}H_8 + 2C_2H_2 \\ 2C_7H_8 \end{cases} &\begin{aligned} &= C_{14}H_{10}, \text{ anthracene, } + H_2, \\ &= C_{14}H_{10}, \text{ anthracene, } + 3H_2. \end{aligned} \end{aligned}$$

R. D. Schulze[3] explains the formation of hydrocarbons found in coal tar by assuming that the phenols are the primary products, and that the hydrocarbons are formed from these by the splitting off of the elements of water. But Lunge points out that, considering the fact that the phenols are more stable than the hydrocarbons under the influence of heat, this theory seems scarcely plausible.

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[1] Ber. d. chem. Ges., **10**, 853.

[2] Ber. d. chem. Ges., **11**, 1215.

[3] Ann. Chem. (Liebig), **227**, 143.

Lewes[1] essentially follows Berthelot's theory. According to Lewes the decomposition of ethylene would be explained by the following reactions :

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$
$$2CH_4 = C_2H_2 + 3H_2.$$

Haber,[2] however, takes exception to all former theories. From the results of the exceedingly interesting and important experiments he and Oechelhäuser performed, with hexane and trimethylethylene, mentioned elsewhere, he arrived at the following conclusions: When aliphatic hydrocarbons with more than two carbon atoms in the molecule are heated for some time to between 600° and 800° C. they break up into lower molecules, but free carbon and hydrogen are *never* formed at this temperature. The hydrogen atoms at the point where the break occurs suffer transposition, while the bond between the carbon atoms at that point is broken. Thus, hexane gives methane and amylene, the smaller molecule formed being always a paraffin, the larger an olefin, and the latter, by polymerization, gives more complex molecules. As the paraffins containing but one or two carbon atoms cannot thus decompose without liberating carbon and hydrogen, he placed them in a special class, and condemns Berthelot's work, which was done upon just such hydrocarbons. While the formation of the doubly unsaturated and of the acetylene hydrocarbons is difficult, they are always formed to some extent.

But between 900° and 1,000° C. he found that new reactions took place and more complicated products were formed. Methane was the only paraffin, ethylene the only olefin formed at this temperature. The attraction between carbon and hydrogen weakened, and free hydrogen appeared, along with increased quantities of benzol. The latter he considered a by-product of the reaction which is not formed so long as the carbon-hydrogen attraction is stronger than that of carbon-carbon. Just how far the olefins added hydrogen cannot be said, but it was certain that ethane, propane, etc., were not formed in this way, for they did not occur in the gas. As he found benzol to be formed both from hexane and from trimethylethylene he concluded that its formation must be due to the polymerization of acetylene. He did not, however, accept Berthelot's "equilibrium," for the reactions seemed to run in different directions, and to lead to entirely different results.

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[1] Proc. Roy. Soc., **55**, 91; and **57**, 540.

[2] Ber. d. chem. Ges., **29**, 2691.

We thus see that while several ingenious theories of the pyrogenic reactions have been advanced, no two of them agree with each other, and, as will be seen further on, they offer at the best only a partial and unsatisfactory explanation of a few of the observed facts, while there are many features of these reactions which they do not make clear.

Historically, a consideration of the work which has been done upon the by-products of oil-gas is very interesting. Faraday was apparently the first to investigate the subject, and in 1825 he published a paper "On New Compounds of Carbon and Hydrogen, and on Certain Other Products Obtained during the Decomposition of Oil by Heat."[1] In this paper he described a new compound which he called "Bicarburet of Hydrogen," now known as "Benzol," and also another new compound, analysis of which showed carbon and hydrogen in the same proportion as in olefiant gas, but whose density was twice that of the latter. This is the composition of butylene, whose discovery has hence always been attributed to Faraday. Both of these new compounds he found in the tar from oil-gas, and his memoirs show that the gas of 1825, made from fish or vegetable oil, differs little from that of to-day, made from petroleum.

Berthelot, in 1867, was the next whose work was connected with this subject. Perhaps his most important experiments were those with acetylene.[2] By the action of relatively low heat upon acetylene enclosed in glass tubes over mercury, he obtained both solid and liquid condensation-products, among which he identified benzol, styrol, naphthalene, and hydrogen. By passing the gas through red-hot porcelain tubes he obtained considerable naphthalene, along with hydrogen, the olefins, and methane. These are among the experiments upon which he based his theory of the pyrogenic reactions, mentioned before.

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[1] Phil. Trans., 1825, 440.

[2] Ann. Chim. Phys. [4], 9, 445.

In 1877, Letny,[1] after a preliminary and doubtless incomplete investigation of the subject, came to the somewhat erroneous conclusion that the tars obtained by the dry distillation of wood and from the manufacture of oil-gas have the same composition. Continuing his work later, Letny[2] employed a petroleum residue from Baku of 0.870 specific gravity, which started to boil at 270°. He conducted the vapors of this oil through red-hot tubes 7 feet long, filled with wood charcoal. The first tar obtained went through the operation again. In this way he obtained a tar whose specific gravity was 1.027 and which was equivalent to 40 per cent. of the oil taken. He gives the composition of this tar as follows: 2.3 per cent. water; 4.6 per cent. benzol; 5.2 per cent. toluol and xylols; 26.9 per cent. naphthalene; 2.7 per cent. phenanthrene; 2.4 per cent. anthracene; 23.1 per cent. unchanged petroleum; and 20.6 per cent. pitch. These percentages doubtless represent crude products, for he makes no mention of unsaturated hydrocarbons, which are always present in these tars.

In 1878, about the same time that Letny was experimenting, Liebermann and Burg were employed upon similar work.[3] In the tars obtained by passing brown coal tar (which, as said before, consists mainly of paraffins) through red-hot tubes they identified benzol, toluol, naphthalene, and anthracene, while from a petroleum treated in the same way they obtained benzol, but scarcely any naphthalene.

Liebermann and Burg were the first to investigate the effect, upon the product obtained, of different substances when placed in the tubes. They experimented first with empty tubes, then with tubes filled with charcoal, with coke, and with pumice stone. In every case the charcoal gave the best results, while the empty tubes gave the worst. They attributed the good effects of such fillings to the greater extent of surface afforded. Letny came to a similar conclusion after comparing the results obtained by using empty tubes of different diameters, then these same tubes filled with charcoal and with platinum black. The latter gave the best results and the wide empty tubes the poorest.

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[1] Bull. Soc. Chim., 1877, 554.

[2] Ding. Jour., **229**, 353; and **231**, 190.

[3] Ber. d. chem. Ges., **11**, 723.

Salzman and Wichelhaus[1] conducted experiments similar to those of Liebermann and Burg, arriving at the same conclusion as regards the filling of the tubes with charcoal and various other substances. Furthermore, they mixed air, acid vapors, etc., with the vapors of the hydrocarbons employed, but obtained no noticeable effect on the resulting tars. They used a brown coal tar, which commenced to boil at 250°, and compared the different results obtained by using eight different fillings for the tubes. The resulting tars varied from a yield of 43 per cent. and a specific gravity 0.9316, obtained by using very large gas coke, up to a yield of 67 per cent., and a specific gravity 0.8869, obtained by the use of platinum asbestos.

Lunge,[2] in 1879, conducted petroleum residues through red-hot tubes, and identified in the product, benzol, toluol, naphthalene, and anthracene.

Williams,[3] in the liquid deposited during the compression of Pintsch gas, found benzol and toluol, ranging in percentage from 25 to 66.

Redwood,[4] by passing the vapors of a petroleum residue through red-hot tubes obtained benzol, naphthalene, and anthracene.

Brochet,[5] in compressed Pintsch gas, identified normal butylene, normal amylene, normal hexylene, and piperylene.

Nikoforoff,[6] by conducting naphtha through red-hot tubes, obtained 12 per cent. benzol and toluol, 0.5 per cent. anthracene, 2.0 per cent. naphthalene, and a tar described as "consisting of hydrocarbons."

Norton and Andrews,[7] by conducting normal hexane through red-hot tubes, obtained ethylene, propylene, crotonylene, amylene, hexylene, and benzol, but no acetylene. From isohexane, at the same temperature, no benzol was formed, but the other products were similar to those from normal hexane. Normal pentane, at a red heat, gave no benzol.

[1] Ber. d. chem. Ges., **11**, 1431.

[2] Industrie des Steinkohlentheers, p. 79.

[3] Chem. News, **49**, 197.

[4] J. Soc. Chem. Ind., 1885, 79.

[5] Compt. rend., **114**, 601.

[6] Eng. Pat. 10,957, 1886.

[7] This JOURNAL, **8**, 1.

Norton and Noyes,[1] by passing ethylene through red-hot tubes, obtained benzol, naphthalene, propylene, butylene, crotonylene, methane, but no acetylene, and from this work they question whether benzol is formed from acetylene, their own theory being that it owes its formation to the olefins.

So far as the actual by-products of oil-gas are concerned, the work of Armstrong and Miller[2] is the most thorough and complete yet done upon the subject. They employed the three different products from the Pintsch gas plants of England—the tar, the gas, and the liquid deposited during the compression of the gas. In the tar they identified benzol, toluol, the xylols, mesitylene, pseudocumene, and naphthalene; in the gas and compressed liquid, crotonylene, valerylene, ethylene, propylene, amylene, hexylene, and heptylene. They assert that in their products there were no true acetylenes, no diphenyl, no olefins higher than heptylene, and no butylene.

Rudnew[3] describes a plant in Russia where benzol is recovered on a commercial scale from oil-gas tar.

Hlawaty[4] passed steam heated to 400° through petroleum, and conducted the vapors produced through red-hot tubes. In a distillate obtained in this way he identified benzol, toluol, xylols, cumol, cymol, styrolene, and anthracene. Acetylene was present in the gas.

Lewes,[5] in the tar obtained by passing the vapors of a Russian oil through red-hot tubes, identified hexane, heptane, nonane, hexylene, heptylene, and benzol.

The most recent, and at the same time probably the most scientific and important work done upon the pyrogenic reactions, was that of Haber and Oechelhäuser[6] upon the decomposition of hexane and of trimethylethylene at different temperatures. The vapors of the hydrocarbon were conducted through a porcelain tube enclosed in a tube of platinum iridium, the latter being heated by the resistance it opposed to the passage of a constant and powerful electric current. The temperature of the retort could thus easily be controlled.

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[1] This JOURNAL, **8**, 362.

[2] J. Chem. Soc., **49**, 74.

[3] Ding. Jour., **239**, 72.

[4] German Pat. 51.553.

[5] J. Soc. Chem. Ind., 1892, 584.

[6] J. of Gas Lighting, 1896.

Between 600° and 700° no decomposition took place, the hydrocarbons first starting to decompose between 780° and 810°. Between 900° and 1,000°, hexane gave the following products: 27.77 per cent. methane; 22.14 per cent. olefins; 1.1 per cent. acetylene; 2.44 per cent. hydrogen; 6.76 to 10.0 per cent. benzol; 3.27 per cent. coke; 29.22 per cent. tar, with a trace of naphthalene. They concluded that, in consideration of their small amounts, acetylene, benzol, coke, and hydrogen could be but side products of these reactions. They attempted to nitrate the tar without removing the unsaturated hydrocarbons and it immediately "carbonized," as it naturally would under these circumstances. Without further investigation they at once concluded that the tar was composed of "condensed olefins." They set 940° as the limit beyond which hexane cannot be heated without considerable decomposition into carbon and hydrogen.

Trimethylethylene, by similar treatment, gave:

1. A similar benzol formation to that of hexane. Since hexane and trimethylethylene have no long chain in common, they concluded that the formation of benzol must be due to polymerization of acetylene.

2. At 935°, more methane than the splitting off of only one CH_3 could account for.

3. Hydrocarbons with closed chains, which, however, were formed with more difficulty than they were from hexane.

Between 668° and 790° they obtained a gas similar to that from hexane, and no separation of carbon and hydrogen could be observed. The tar contained only those olefins which have greater molecular weight than trimethylethylene, while the absence of all higher paraffins they consider especially remarkable. Between 933° and 938°, trimethylethylene gave the following products:

27.72 per cent. methane; 8.10 per cent. ethylene; 1.76 per cent. hydrogen; 4.46 per cent. other gases; 0.30 per cent. acetylene; 5.09 per cent. coke; 8.0–13.4 per cent. benzol; 33.71–39.12 per cent. tar, more methane and benzol being formed at this higher temperature, as was also the case with hexane. They set 950° C. as the limit to which trimethylethylene can be heated before starting to decompose into carbon and hydrogen.

By conducting benzol itself through the retorts they found that it did not start to decompose until the temperature was between 900° and 1,000°, and that the tar thus obtained differed considerably from that given by hexane and trimethylethylene at the same temperature. Hence, they concluded that the compounds in the latter tars must have been condensation-products of benzol, ethylene, etc., rather than decomposition-products of benzol.

We thus see that while considerable work has been done upon the products of the decomposition of paraffin hydrocarbons at high temperatures, the results so far attained, in comparison with those arrived at in the case of coal tar, are meager and in some cases contradictory and unsatisfactory. The following is a summary of all the compounds which have ever been identified in the products arising from such treatment of aliphatic hydrocarbons:

Benzol
Toluol
Xylols
Mesitylene
Pseudocumene
Cumol (?)
Cymol (?)

Naphthalene
Anthracene
Phenanthrene

Ethylene
Propylene
Butylene
Amylene
Hexylene
Heptylene

Acetylene
Crotonylene
Piperylene
Styrolene (?)

Methane
Hydrogen

[We have purposely omitted in the preceding review the results obtained by the simple distillation of petroleum residues, which leads to the formation of "still-wax," believing that they belong rather under the head of the "cracking" of petroleum than to the subject we are discussing. "Cracking" of petroleum seldom or never exceeds 450° C., the only "pyrogenic" reactions taking place in the coke when the latter is heated to redness.]

Considering the fact that the "pyrogenic" reactions have been under investigation for nearly seventy-five years, the progress which has been made is not very great. So many investigators have been content simply to repeat the work of former chemists, and do not know, or at least do not state, the composition of the oil employed, nor make their work quantitative. This is unfortunate, for the question is one which deserves careful consideration, and which offers an almost unlimited field for investigation.

In reading over the literature of the subject one can scarcely fail to be impressed by one peculiar fact, namely, that the products obtained by the action of red heat upon the paraffins *are always the same, no matter what particular hydrocarbons are employed for the experiment.* Now, while coal and petroleum differ in percentage composition they are composed of the same elementary material, and the question suggested itself: Will not petroleum, when treated by destructive distillation, yield a tar exactly similar to coal tar, varying from the latter only in percentage composition? It was in order to investigate this question, and also, if possible, to throw some additional light upon the pyrogenic reactions, that the work described in this paper was undertaken.

In choosing crude heptane and octane as the material to be employed for the experiment, we were influenced by several considerations. In the first place, so far as we are aware, no investigation has ever been made of the decomposition-products of these two hydrocarbons, while those of pentane and of normal and isohexane have received some attention. The crude hydrocarbons were selected in order that the sulphur, nitrogen, and oxygen bodies being still retained, the similarity of the resulting tar to that of coal might be investigated. And we were further influenced in our choice by the fact that the Pintsch plant of the Cleveland Gas Light and Coke Co. was employing exactly the material we had selected, and their treatment of the oil in the retorts was much more complete than we could hope to attain in a laboratory experiment. Through the kindness of this company and of the Recovery Oil Co., which employs their tar, we were able at all times to obtain any material we desired in large quantities. That this was a considerable help may readily be imagined.

The Material Employed.

The heptane and octane employed for the experiment was ordinary 63° naphtha, whose actual gravity at 15° was 0.7310. An assay of this naphtha gave the following figures:

Fraction.	Per cent.
90°–100°	11.0
100°–110°	30.0
110°–120°	27.0
120°–130°	18.0
130°–139°	14.0
	100.0

As hexane boils at 69° and nonane at 150°, there could not have been more than traces of these two hydrocarbons in the heptane and octane, even if present at all. That this naphtha was quite free from impurities was shown by determination of the bromine-absorption and the percentage of sulphur.

In determining the amount of sulphur present, the lamp method of combustion was employed.

1.5860 grams oil required 1.0 cc. of $\frac{1}{10}$-normal NaOH, equivalent to 0.001 gram, or 0.063 per cent. sulphur.

In determining the bromine-absorption a weighed quantity of the oil was placed in a perfectly dry glass-stoppered bottle, dissolved in 15 cc. of carbon tetrachloride, and 10 cc. of a solution of bromine in carbon tetrachloride added. The bottles were then tightly stoppered and left in the dark over night. 25 cc. of a 10 per cent. solution of potassium iodide were then added, and the iodine thus liberated titrated with $\frac{1}{10}$-normal sodium thiosulphate, with the aid of starch paste. Then 15 cc. of a saturated solution of potassium iodate were added. The iodine thus set free by the hydrobromic acid, which had been formed by substitution, was titrated with more thiosulphate.

$\left.\begin{matrix}5.3550\\5.8431\end{matrix}\right\}$ grams oil thus treated required $\left.\begin{matrix}30.8\\25.9\end{matrix}\right\}$ cc. $\frac{1}{10}$-normal $Na_2S_2O_3$ after adding KI, and $\left.\begin{matrix}16.8\\19.2\end{matrix}\right\}$ cc. more after adding the iodate. A blank run at the same time, using the same amount of carbon tetrachloride and bromine solution, required 67.2 cc. $\frac{1}{10}$-normal thiosulphate before adding the iodate, and 8.0 cc. after this addition (this high substitution-figure was due partly to chloroform in the tetrachloride, and, mainly, to acidity of the potassium iodate solution).

Hence, $\left.\begin{array}{l}67.2-30.8=36.4\\ 67.2-25.9=41.3\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine were used both in adding and in substituting, and $\left.\begin{array}{l}16.8-8.0=8.8\\ 19.2-8.0=11.2\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine for substituting. And since, for every bromine atom which substitutes, one molecule of hydrobromic acid is liberated, $\left.\begin{array}{l}36.4-(2\times 8.8)=18.8\\ 41.3-(2\times 11.2)=18.9\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine were used in addition. This gives a result of $\left.\begin{array}{l}2.80\\ 2.61\end{array}\right\}$ per cent. bromine added, and $\left.\begin{array}{l}1.32\\ 1.52\end{array}\right\}$ per cent. bromine substituted.

Treatment of the Heptane and Octane.

The technology of the manufacture of gas from petroleum by the Pintsch process is very simple, and differs only in a few minor details at the various works. The process in use at the Pintsch plant of the Cleveland Gas Light and Coke Co., and by which the naphtha just described was treated, is briefly as follows: The retort consists of a cylinder of cast iron, perhaps 10 feet long and 6 inches in diameter, enclosed in the ordinary clay retort of the gas works, the whole being heated to about 900° C. The iron cylinder consists of three shells or tubes. The oil enters from an exterior pipe in front, drop by drop, into the inner tube, and is at once vaporized. The vapors, after passing through the inner tube, encounter a cap on the end of the next larger tube, which encloses the inner, traverse it in the opposite direction, strike a cap on the front of the largest enclosing tube, and after traversing its length emerge in the rear of the clay retort, which they must pass through in order to make their exit into the hydraulic main. This gives a total distance of about 40 feet which the oil vapors must traverse under the influence of the heat. The arrangement of the hydraulic main, condensers, scrubbers, and purifiers is exactly the same as for coal gas. Very little work is done, however, by any of these save the hydraulic main, which removes the tar, for the impurities found in coal gas are nearly absent from the gas made from oil. After purification the gas is compressed by pumps into welded steel cylinders, perhaps 20 feet long and 5 feet in diameter, where it is kept under a pressure of from 15 to 17 atmospheres.

The Products.

When heptane and octane are treated in the manner just described, they yield as products:

1. A small quantity of a very hard graphitic coke, deposited on the outside of the iron retort.
2. The tar, deposited in the hydraulic main, and equivalent to 25 per cent., by weight, of the original oil.
3. A liquid, designated by the gas men as "hydrocarbon," deposited during the compression of the gas and equivalent to about 10 per cent. by weight of the original oil.
4. The gas itself.

While the actual composition of the tar, as shown by a number of assays, seems to be always the same, the percentage composition varies. This seems to be due to the varying amounts of lower-boiling hydrocarbons which the hot gas carries through the hydraulic main, and which are deposited further on when the gas is compressed. The particular tar which was employed in this research assayed as follows:

The specific gravity at 15° was 0.9369 as opposed to that of the original oil, 0.7310, at the same temperature.

22.5 liters of this tar, when distilled, gave the following products:

		Per cent.
78°–112° (benzol and toluol)	7500 cc.	34.0
112°–200° (xylols, etc.)	3000 cc.	14.0
200°–250° (crude pressed naphthalene)	2600 grams	11.7
200°–340° (oils)	3200 cc.	14.2
Crude pressed anthracene	520 grams	2.3
Solids above anthracene	220 "	1.0
Oils above 340° (containing anthracene)	1000 cc.	4.8
Pitch residue (above 450°)	3260 grams	15.0
		97.0

The bromine-addition of the tar was determined in precisely the same way as that of the original naphtha.

0.2773 gram of the tar was dissolved in 15 cc. carbon tetrachloride and 10 cc. of the bromine solution added. After standing over night, it required 42.8 cc. $\frac{1}{10}$-normal $Na_2S_2O_3$ after adding KI and 14.4 cc. more after adding KIO_3. This gives the bromine-addition 34.48 per cent. and the substitution 18.88 per cent.

The liquid which is deposited during the compression of the gas consists of the lower-boiling hydrocarbons of the tar taken up by the hot gas in its passage through the hydraulic main. The average of a number of assays of this liquid showed about 6 per cent. unsaturated hydrocarbons from 20° to 78°; 80 per cent. of benzol between 78° and 100°; and 10 per cent. toluol and xylols, the loss of 4 per cent. being due to gas dissolved in the liquid. The gas itself will be described further on.

The Aromatic Series.

Nearly every investigator of oil-gas tar has found benzol and toluol, and several have identified the xylols. Armstrong and Miller found mesitylene and pseudocumene, and Hlawaty identified cumol and cymol, but the method of the latter was somewhat irregular. No other hydrocarbon of this series, so far as we know, has ever been identified in the decomposition-products of the paraffins.

For our investigation of the members of this series, 22.5 liters of the tar were distilled from a copper still holding 12 liters, and specially constructed for tar distillation. Up to 270° dry distillation was employed in fractions of 5° each, then the residue distilled with highly superheated steam as long as any distillate would come over. In this way distillates were obtained whose boiling-points ran considerably over 400°. Solid distillates were all cold-pressed and the oils drained off. The separate fractions were then treated in the cold with one per cent. of concentrated sulphuric acid at a time until free from all unsaturated hydrocarbons, washed with water and caustic soda, and dried, It was found that about 6 per cent. concentrated sulphuric acid was required for thorough treatment. All these treated distillates were then repeatedly fractioned, with the aid of Hempel columns, until the right separation was attained.

Benzol.—The fraction boiling from 79°-82° was twice frozen, and the residual oil drained off from the benzol crystals. The benzol thus obtained had a specific gravity of 0.8810 at 10° C., and gave no coloration with strong sulphuric acid, showing its purity.

A quantity of this pure benzol was nitrated, the nitro product washed with water and caustic soda, then distilled with steam. The nitrobenzol thus obtained was a very faintly yellow liquid, which boiled at 205°-206°, and whose specific gravity was 1.203 at 15°, both being correct for pure nitrobenzol. The total quantity of benzol present in this tar was about 18 per cent.

Toluol.—The specific gravity of the 109°-112° fraction was 0.8603 at 15° C. It was nitrated and the nitro products washed and distilled with steam. This distillate was dried and fractioned. The orthonitrotoluol boiled at 223°-225°, was faintly yellow, and its specific gravity was 1.157 at 15°, showing its purity. The percentage of toluol in the tar was about 12.

Xylols.—A cold mixture of sulphuric and nitric acids, shown by Jacobsen to be capable of distinguishing a very minute quantity of orthoxylol in a mixture of the three, immediately gave in the 135°-145° fraction an oily layer between the acids and the hydrocarbons, showing the presence of orthoxylol.

For the detection of meta- and paraxylols, the following method, which we have not found described elsewhere, gave fair results: About 50 cc. of the mixed xylols were gently heated for some time with a mixture of chromic and sulphuric acids in a flask with return condenser. By this treatment orthoxylol is completely burned to carbon dioxide and water, metaxylol gives isophthalic acid, paraxylol gives terephthalic acid. When oxidation was completed the mixture was poured into cold water, and the precipitated acids filtered and washed with cold water, then dissolved in caustic soda and reprecipitated with hydrochloric acid, this being repeated until the acids were obtained pure. They were then dissolved in ammonia and the solution just neutralized with hydrochloric acid. Barium chloride was then added in the slightest possible excess, precipitating all the terephthalic acid as barium terephthalate. This was filtered and hydrochloric acid added, in excess, to the filtrate precipitating isophthalic acid.

While attempting to secure further proof of the presence of meta- and paraxylols by forming the sulphonic acids, we, unfortunately, lost the rest of this fraction, and, having no more of this distillate, could make no further tests. But we think there can be no doubt of the presence of the three xylols. Their percentage in the tar was about 5.

The members of the aromatic series boiling above 150° are still under investigation, and will receive further attention. We may state, however, that we have fractions of highly refractive liquids, boiling all the way from 150° to above 300°, and we hope soon to be able to determine the composiof these distillates, which are equivalent to 20 per cent. of the tar.

Compounds with Condensed Benzol Nuclei.

Naphthalene, anthracene, and phenanthrene were the only members of this series which had ever been identified in such tars.

Naphthalene.—The distillate between 200° and 250° was cooled and the solids pressed free of oils. This crude pressed naphthalene was quite pure, its melting-point being 78°. When sublimed it gave the proper melting-point, 79°. The percentage of naphthalene in this tar was 11.8.

In fractioning the oils between 150° and 300°, some naphthalene was contained in all the distillates from 200° to 260°. As diphenyl boils at 254°, it was thought that it might be contained in the solids of the 250°–255°, and 255°-260° fractions. But the latter, when drained and pressed, melted at 78°, and, when recrystallized from hot alcohol, at 79°, showing it to be naphthalene. Diphenyl melts at 71°, and its presence here could hardly have failed to change the melting-point of the naphthalene. While diphenyl has often been sought for in the oil-gas tars it has never been found. It seems rather curious that it should not occur along with the other condensed-ring hydrocarbons.

Anthracene.—The solid which came over with steam after the oils above naphthalene had distilled was a yellow oily mass. The oils were removed by cold-pressing, and the crude anthracene thus obtained was a butter-yellow.

50 grams were dissolved in glacial acetic acid and oxidized with 90 grams chromic acid, the excess of acetic acid distilled off, and the residue poured into water. The brown precipitate was filtered and washed with water, then warmed with a solution of acid sodium sulphite to remove phenanthraquinone, filtered, and washed with water. The residual anthraquinone was dried and sublimed, giving the characteristic golden needles of anthraquinone, melting at 285°. The amount of anthracene present in the tar was about 3 per cent.

Phenanthrene.—Dilute sulphuric acid, when added in slight excess to the solution in acid sodium sulphite, gave a yellow precipitate. This was filtered, washed, and dried, and then crystallized from hot benzol. The phenanthraquinone thus obtained had a constant and correct melting-point, 198°. There was about 0.4 per cent. phenanthrene in the tar.

Chrysene.—The steam distillate above anthracene was an oily, reddish-yellow solid. It was pressed and then washed with petroleum ether to remove all oil. The solid thus obtained was a yellow meal. This solid was repeatedly extracted with carbon disulphide and filtered. The residue was greenish-white, very sparingly soluble in hot alcohol, and somewhat readily soluble in hot benzol, the latter solution having the beautiful violet fluorescence characteristic of chrysene. It was repeatedly crystallized from hot benzol, separating in small greenish-white leaflets. The melting-point remained constant at 250°, which is correct for chrysene. To still further identify the chrysene, it was dried, and a portion oxidized to the quinone by suspending it in glacial acetic acid, adding chromic acid slowly, boiling after each addition, and filtering while boiling hot. The filtrate, when diluted with water, gave an orange-red precipitate, which was filtered and washed. A single particle of this quinone with concentrated sulphuric acid, gave the deep blue color so characteristic of chrysenequinone. There was about 0.4 per cent. chrysene in the tar.

Fluoranthene?—The carbon disulphide solution obtained upon extracting the chrysene was distilled, and the residue extracted again with a little carbon disulphide. It was found that more chrysene was obtained by this treatment, which was continued until all the chrysene had been removed. A small portion of the residue, which was yellow, when dissolved in warm sulphuric acid, gave the deep blue fluorescence said to characterize fluoranthene, but there was not enough of it to enable us to further identify it.

Aliphatic Hydrocarbons.

Armstrong and Miller,[1] in forming the sulphonic acids of the benzol fraction of Pintsch-gas tar found that not all of the hydrocarbon would dissolve in fuming sulphuric acid, and this residue, after distillation in steam over a little alkali, they describe as a clear, brilliant oil with the "sweet odor of a true paraffin." They did not have enough of this oil to enable them to identify it, but concluded that it was composed both of paraffins and "pseudolefins," or the so-called naphthenes. It is probably upon the strength of this surmise that Lunge[2] makes the incorrect statement that Armstrong and Miller found the naphthenes in Pintsch-gas tar.

In the course of our work upon the aromatic series in the tar we found just such an oil as Armstrong and Miller describe, and went to considerable pains to determine its nature. It was noticed that upon nitrating benzol and then distilling in steam, the first distillate was a brilliant oil of low specific gravity, amounting to not more than 4 per cent. of the hydrocarbon taken, and insoluble in fuming sulphuric acid. Two liters of this distillate were obtained at the works of the Recovery Oil Co., and the hydrocarbons separated by distillation from the nitrobenzol contained. The distillate thus obtained had a peculiar sour smell and the specific gravity 0.7306 at 15° C. It was treated with fuming sulphuric acid in the cold until no further action took place, then washed with caustic soda and water. By this treatment only about 3 per cent. of the oil was removed, the specific gravity remaining practically the same—0.7280 at 15°—but the sourness was removed, leaving a very sweet and pleasant smell.

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[1] *Loc. cit.*

[2] Industrie des Steinkohlentheers.

Upon nitrating 1100 cc. of toluol and then distilling in steam, 90 cc. or 8.2 per cent. of a similar inert oil was obtained, whose gravity was 0.7316 at 15°. This was added to that obtained from the benzol, and the whole of this oil, amounting to about a liter, very carefully fractioned over sodium, finally a number of times at 1° intervals. It all distilled between 90° and 130°, and collected chiefly at 98°-99° and 118°-120°.

Two vapor density determinations of the 98°-99° fraction gave 49.2 and 50.8. Heptane, boiling at 98°-99°, has the vapor density of 50, hexahydrotoluol, boiling at the same point, has the vapor density of 49. The specific gravity of heptane is given by Thorpe as 0.6885 at 15°, while that of hexahydrotoluol is 0.7723 at 0°. The observed specific gravity of our distillate was 0.7219 at 15°, which, while higher than that assigned to heptane, yet agrees closely with those observed for the same distillates of American petroleum. In order to determine whether, as is thought by many to be the case in petroleum distillates, this heptane fraction owed its higher specific gravity to the presence of a naphthene, portions were boiled with a mixture of sulphuric and nitric acids for definite periods, and the specific gravities of the original and residual oils compared. But in no single instance, even after two-thirds of the original oil had been destroyed, was the least change in the specific gravity noted. Carbon and hydrogen determinations in this fraction gave the following results:

0.1540 gram oil gave 0.4727 gram CO_2, and 0.2230 gram H_2O.

	Calculated.	Found.
$\left\{\begin{array}{l}C_7\\H_{16}\end{array}\right.$	84.00 16.00	83.71 16.08
$\left\{\begin{array}{l}C_7\\H_{14}\end{array}\right.$	85.71 14.29	....

All these results tend to show that the hydrocarbon was normal heptane and that no naphthene was present.

The specific gravity of the octane boiling at 119°, is

0.7188 at 0°, that of hexahydroisoxylol, boiling at 118°, is 0.7814 at 0°. The observed specific gravity of our distillate, 118°–120°, was 0.7292 at 15°. The action of sulphuric and nitric acids caused no noticeable change in specific gravity even after 55 per cent. had been destroyed, and a combustion gave the following results :

0.1864 gram oil gave 0.5781 gram CO_2, and 0.2615 gram H_2O.

	Calculated.	Found.
C_8	84.21	84.54
H_{18}	15.79	15.58
C_8	85.71	....
H_{16}	14.29	....

Hence, this fraction was octane and no naphthenes could have been present.

While treating these hydrocarbons with sulphuric and nitric acids, as before described, some interesting facts were noted. Thus, heptane, after being boiled for an hour with the acid mixture, gave in the wash water of the residual oil the characteristic odor of butyric acid, while upon another occasion valerianic acid seemed to be formed. While numerous chemists have noticed these reactions during their investigation of the composition of petroleum,[1] it is still a question as to just what reactions take place and what products are obtained by the action of these acids upon the paraffins.

In treating the octane fraction in this way, 100 cc. of the oil were gently boiled with 100 cc. sulphuric and 100 cc. nitric acids for fourteen hours. The liquid, on cooling, separated into three distinct layers. The lower layer of acids was drawn off and afterwards thrown away by mistake. The upper two layers were shaken with water, causing the separation of an oily, nitro-like body, whose gravity was nearly that of water.

The residual hydrocarbon was yellow and was extracted with strong sulphuric acid until colorless. It had been found in previous experiments that while caustic soda acted but slowly in extracting these compounds, sulphuric acid worked readily, taking a deep-red color from the extracted body. The sulphuric acid extract was poured into water, cooled, extracted with ether, and the ether distilled off. The residue was a yellow, fatty-smelling compound. 5.44 grams of this were dissolved in alcohol and titrated with 37.8 cc. of normal alcoholic potassium hydroxide. Calculating it as an acid and as monobasic, this gives 143.9 as the molecular weight. The molecular weight of octoic acid is 144. The copper salt was formed and crystallized well, but no further work was done upon it.

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[1] Beilstein and Kurbatow: Ber. d. chem. Ges., **13**. 2028; Mabery: Proc. Am. Acad., **32**, 6.

The heavy nitro-like body before mentioned was tested with potassium hydroxide, potassium nitrite, and sulphuric acid for a nitroparaffin. But the solution in potassium hydroxide gave such an intense red color in itself that the test proved nothing. By dissolving a weighed quantity in alcohol, adding excess of normal potassium hydroxide, and titrating back with normal hydrochloric acid, it was found to be a neutral compound.

Konowalow[1] obtained nitrohexane by heating normal hexane to 135° with nitric acid af 1.075 specific gravity. Beilstein and Kurbatow[2] made nitroheptane by boiling the 95°–100° fraction of American petroleum with nitric acid of specific gravity 1.38. It is possible that the compounds we obtained from octane by this treatment with sulphuric and nitric acids were nitrooctane and octoic acid. While the whole subject is very interesting, and one which deserves more attention, it was outside the scope of our subject and was not further investigated.[3]

The presence of aliphatic hydrocarbons having thus been proved, the question arose: Did merely the unchanged heptane and octane occur in the products, or were there lower paraffins also, formed by the decomposition of the two former? As we have seen, nearly every theory of the pyrogenic reaction is based upon the assumption that the higher paraffins split up into lower molecules of the same series. Now, if heptane and octane are able to pass through these red-hot retorts unchanged, as we found to be partly the case, any lower paraffins which are still more stable would certainly be able to do the same. Hence, if lower paraffins are formed, they would necessarily be present to some extent among the products.

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[1] Ber. d. chem. Ges., **25**, [2] 198.

[2] Ber. d. chem. Ges., **13**, 2029.

[3] The action of these reagents upon the paraffins is now being carefully investigated by the author.

The liquid which was noticed as being deposited during the compression of the gas, commences to boil at a very low temperature, and upon being warmed, gives off a considerable amount of gaseous hydrocarbons. The gas given off upon starting a still holding 2,000 gallons of this liquid at the works of the Recovery Oil Co. was passed into two pounds of bromine, kept cool and in the dark. But no gas passed through the bromine even after a rapid stream had been running for several hours. Hence, nothing but unsaturated hydrocarbons could have been present in this lower-boiling portion of the liquid. And upon testing that portion of the liquid itself which boils between 20° and 78°, nothing was found which was insoluble in fuming sulphuric acid, nor was there anything in the distillate above 130° insoluble in the acid. Hence no other paraffins than the original heptane and octane were present in the tar and compressed liquid. The discussion of their presence in the gas itself will be found further on.

Naphthenes.

So far as we could find, no work whatever had ever been done upon the occurrence of naphthenes in oil-gas tar. Although we had proved their absence from that inert hydrocarbon which could not be nitrated or dissolved in fuming sulphuric acid, and which Armstrong and Miller assumed to contain naphthenes, this was not conclusive proof of their absence from the products, for, according to Beilstein, a mixture of sulphuric and nitric acids, when heated, gives with the naphthenes the nitro compounds of the corresponding aromatic hydrocarbons. And where this nitration is carried on with large quantities of the hydrocarbons, and in a commercial way, as is the case at the works of the Recovery Oil Co., the mixture is almost sure to become heated. Then, too, it seems to be a disputed question as to whether or not the naphthenes are soluble in fuming sulphuric acid in the cold, and it was thought best to determine their presence in or absence from the original tar.

For hexahydrobenzol boiling at 69°, 2 liters of a distillate 68°–70° from the compressed "hydrocarbon" were treated in the cold with an excess of concentrated sulphuric acid until all unsaturated hydrocarbons were removed. The residue, of which there was about one liter, was washed with water and caustic soda, dried, and fractioned. Only 50 cc. distilled below 78°, the rest being benzol. The lower distillate was again treated with sulphuric acid, washed, and dried. Repeated fractioning showed this to be benzol, and nothing would distil below 77°. For hexahydrotoluol, boiling-point 97°, and hexahydroisoxylol, boiling-point 118°, 15 liters of the distillate which comes off the tar with tight steam coil, and which are equivalent to about 60 liters of tar, were employed. This was first distilled at 10° limits, then thoroughly treated with sulphuric acid, washed, and dried. The treated distillates were then repeatedly fractioned, first at 5° then at 3° intervals, finally a number of times at 2° limits. A final fractioning showed the following results between 94° and 100°.

	Volume. cc.	Per cent. in tar.	Specific gravity at 20° C.
94°–96°	100	0.17	0.8620
96°–98°	90	0.15	0.8606
98°–100°	70	0.12	0.8588

The specific gravity of hexahydrotoluol is 0.7723 at 0°, and the presence of any appreciable amount would have increased the volume and lowered the specific gravity of the 96°–98° fraction. But both the volume and the specific gravity show only the normal decrease from the benzol to the toluol fractions.

Similarly, no bunching or decrease in specific gravity could be observed in the 118°–120° fraction, where hexahydroisoxylol should occur. Considering the large amount of tar employed and the careful fractioning, it seems certain that no naphthenes were present in the products.

Unsaturated Hydrocarbons.

As shown by the bromine absorption of the tar—33.48 per cent.—unsaturated hydrocarbons are present in considerable amount. These unsaturated hydrocarbons of the gas, the tar, and the compressed liquid will be investigated soon.

The absence of true acetylenes in the tar and compressed liquid has been established, however, by passing the gas from 2,000 gallons of the compressed liquid through ammoniacal cuprous solution. After running at a rapid rate for several hours the gas failed to give any indication of acetylenes, and the liquid itself, when tested with the solution, also gave a negative result.

Oxygen, Nitrogen, and Sulphur Compounds.

So far as we are aware, no attempt had ever been made even to determine the presence of sulphur, nitrogen, or oxygen in oil-gas tars. The question of the formation of compounds of these three classes seemed to us an important one, for if it could be proved that typical members of these groups were present, the similarity of this tar to coal tar would be established.

Phenols.—The phenols were taken as the type of the oxygen compounds occurring in coal tar, and were tested for in the following manner: The untreated distillates of the 22.5 liters of tar between 145° and 210° were thoroughly extracted with caustic soda. This solution was then made slightly acid with hydrochloric acid, and the unmistakable odor of carbolic acid at once became apparent. This slightly acid solution was then extracted with ether, and the ether distilled off from the extract, leaving 1.2716 grams or 0.05 per cent. phenols. This is equivalent to about a pound per ton of tar.

Ferric chloride in neutral solution of this residue gave a violet coloration, and bromine water caused a yellow precipitate of tribromphenol. Hence, carbolic acid was present, and although there was not enough material to test for the higher homologues, it is probable that they also occur in the tar.

Ammonia.—Ammonia was taken as the type of the nitrogen compounds of coal tar. In order to test for ammonia, 2 liters of the water which flows through the scrubbers of the Pintsch-gas works in a small but continuous stream were obtained at the exit. This water showed a faint alkalinity. 500 cc., when titrated, required 0.3 cc. $\frac{1}{16}$-normal hydrochloric acid, equivalent to 0.00006 per cent. free ammonia, or thirty times the amount contained in the lake water itself. The 2 liters of water were made slightly acid with sulphuric acid and evaporated to a small volume. A slight excess of caustic soda was then added, and two-thirds distilled off into 30 cc. of the standard hydrochloric acid. 1.3 cc. of this $\frac{1}{16}$-normal acid were required, which gave 0.000068 per cent. total ammonia. Hence the ammonia was practically all present in the free state.

The percentage of nitrogen in the tar was determined by the Kjeldahl method.

4.2739 grams tar required 2.5 cc. $\frac{1}{16}$-normal hydrochloric acid, equivalent to 0.053 per cent. ammonia, or 0.042 per cent. nitrogen. A qualitative test of the tar for ammonia failed to show the least trace. Hence there are probably nitrogen bases formed in addition to the ammonia.

Sulphur Compounds.—In determining the amount of sulphur present in the tar, it was found that a sufficiently high temperature for complete combustion could not be attained in a combustion furnace without the use of oxygen, and that the lamp method gave good results.

0.9374 gram tar by the latter method gave 0.0005 gram sulphur or 0.053 per cent.

Thiophene was tested for in all the distillates of crude benzol with isatine and sulphuric acid, but could not be detected. In the water which is drawn off with the tar from the hydraulic main, lead acetate failed to give any blackening, but in another portion the addition of a little caustic soda and sodium nitroferricyanide gave the characteristic purple color showing the presence of hydrogen sulphide.

The Gas.

In determining the composition of the gas formed by the heptane and octane, the chief object in view was to investigate the presence of hydrogen, acetylene, methane, and the higher paraffins. The formation of hydrogen and acetylene by the pyrogenic reactions is still a disputed question. J. B. Lewes,[1] in the gas obtained by passing Russian petroleum through tubes heated to between 900° and 1000°, found from 12 to 22 per cent. hydrogen, and from 0.38 to 0.46 per cent. acetylene. Pryce and Hunt,[2] by passing Russian oil through retorts whose temperatures varied from 600° to 1060°, found hydrogen *always* present in the gas, ranging in percentage from 16 to 57, along with from 23 to 51 per cent. methane. Haber and Oechelhäuser,[3] however, assert that from hexane they obtained no hydrogen until the temperature reached 900°, and between 900° and 1000° only 2.44 per cent. along with 1.10 per cent. acetylene and 27.77 per cent. methane, while Norton and Andrews,[4] from normal and isohexane, could obtain no acetylene. While there thus seem to be conflicting opinions about the formation of hydrogen and acetylene from paraffins under the influence of heat, methane is always found in considerable quantity and *never associated with higher homologues.*

A large gasometer full of the gas made from the heptane and octane was obtained directly from the compression tanks of the Pintsch plant, and its constituents determined in the following way: Carbon dioxide by potassium hydroxide solution; oxygen by pyrogallol; acetylene by ammoniacal cuprous chloride; the other luminants by fuming sulphuric acid; hydrogen by absorption in palladium sponge; and methane by exploding the residue. Carbon monoxide and nitrogen were determined independently; carbon monoxide by first removing all luminants, then absorbing in ammoniacal chloride; nitrogen by exploding this residue.

Considering the high pressure upon the gas, the aromatic hydrocarbons could hardly have been present, or at least only to a very small extent. In determining methane, a measured volume of the gas residue was mixed with a measured volume of oxygen and exploded in a pipette over strong sulphuric acid. The contraction here was due to the water vapors absorbed by the acid, and by passing into potassium hydroxide the amount of carbon dioxide was determined. In every case the volume of oxygen actually used for the explosion was just twice that of the gas taken, less the nitrogen it contained; the volume of carbon dioxide formed was equal to that of the gas less the nitrogen; and the volume of water vapor twice as great, thus showing the residual hydrocarbon to have been all methane, according to the reaction:

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[1] J. Soc. Chem. Ind., 1892, 584.

[2] Gas World, 18, 511.

[3] *Loc. cit.*

[4] *Loc. cit.*

$$\begin{array}{lccccccc} & CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O, \\ \text{Volumes} & 1 & & 2 & & 1 & & 2 \end{array}$$

while from the nature of the reactions of ethane and higher homologues,

$$\begin{array}{lccccccc} & C_2H_6 & + & 3\tfrac{1}{2}O_2 & = & 2CO_2 & + & 3H_2O, \\ \text{Volumes} & 1 & & 3\tfrac{1}{2} & & 2 & & 3 \\ & C_3H_8 & + & 5O_2 & = & 3CO_2 & + & 4H_2O, \text{ etc.,} \\ & 1 & & 5 & & 3 & & 4 \end{array}$$

we see that these higher paraffins could not have been present.

The percentage composition of the gas, taken from the average of several determinations, was as follows:

Nitrogen[1]	11.8
Acetylene[2] (and ethylene?)	11.3
Other luminants	15.5
Hydrogen	18.4
Methane	42.9
	99.9

Summary.

It has been observed at the Pintsch plant that 16 gallons of this naphtha always give about the same quantity of each product—3 gallons of tar, 1.5 gallons of "hydrocarbon," and 1,000 cubic feet of gas. Calculating from these figures and from the specific gravities and percentage composition of these several products, we find that crude heptane and octane, containing small quantities of sulphur, nitrogen, and oxygen compounds, gave, when decomposed at about 900°, solid, liquid, and gaseous products of the following nature and amounts:

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[1] The nitrogen was doubtless due to air introduced by the pumps during the compression of the gas, the corresponding oxygen having been absorbed by the unsaturated hydrocarbons deposited at the same time, which were found to take up oxygen readily.

[2] Hempel has shown that ammoniacal cuprous chloride slowly absorbs ethylene. Hence the figure obtained for acetylenes probably represents some ethylene also, for considerable difficulty was experienced in obtaining satisfactory duplicates of this determination, which was made as rapidly as possible. A large amount of acetylene was present, however, for, whenever the gas was passed into the ammoniacal cuprous chloride, it gave a heavy red deposit of cuproacetylene.

	Percentage by weight.
Olefins	26.0
Methane	25.1
Benzol	12.5
Acetylene (and ethylene?)	12.1
Toluol	3.0
Xylols, etc. (120°–200°)	3.0
Aromatic hydrocarbons (200°–300°)	4.5
" " (above 300°)	2.3
Naphthalene	3.6
Anthracene	1.3
Phenanthrene	0.1
Chrysene	0.1
Fluoranthene(?)	about 0.01
Pitch	4.1
Hydrogen	1.4
Phenols	0.01
Ammonia and nitrogen bases	small amounts
Hydrogen sulphide	" "
Coke	" "
Naphthenes	absent
Thiophene	"
Diphenyl	"
Higher acetylenes	"
Paraffins, other than methane	"
Total	99.1

Upon consulting this table one notices that the olefins, methane, acetylene, and the aromatic hydrocarbons seem to be the chief products of the reaction, for, taken together, they constitute 88.5 per cent. of the total product. The method of their formation, however, is another question. Whether the higher aromatic hydrocarbons are formed directly by the reaction or are only secondary products owing their formation to the decomposition of benzol; whether acetylene is a primary product or is formed by decomposition of the olefins; whether benzol owes its formation to the polymerization of acetylene; of these and many other problems the table gives no solution. We see, moreover, that more methane is formed than the splitting off of only one methyl group from heptane or octane can account for, more hydrogen than the liberation of only one molecule from either hydrocarbon can explain.

We see also that the products yielded by the naphtha are almost exactly identical with those obtained from coal by similar treatment. This does not, however, imply any great similarity between the constitution of coal and of petroleum, for if we review the work which has been done upon the products of the pyrogenic reactions, we are confronted by some peculiar facts. We see that practically the same products were obtained by Letny from petroleum hydrocarbons, none of which could have been below pentadecane, as by Haber from hexane and from amylene; by Haber from hexane and from amylene, as by Berthelot from acetylene; by Norton and Noyes from ethylene, as by Haber from hexane; by Berthelot[1] from toluol, from xylol, and from cumol, as from acetylene; and, finally, by the author from crude heptane and octane, as by Berthelot from the aromatic hydrocarbons, and by countless investigators from coal.

Hence it would seem, *that all hydrocarbons, under similar conditions of temperature, yield the same products*. What theory so far advanced explains all the facts? Schulze's explanation of the formation of coal-tar hydrocarbons from the phenols cannot be correct, for the same hydrocarbons are formed from compounds which contain no oxygen. If Berthelot, Haber, and all the others who explain such reactions by assuming that the paraffins first split up into lower molecules are correct, why are not these lower paraffins found among the products, and why do hydrocarbons which do not belong to the paraffin group—ethylene and xylol, for example—yield the same products as the paraffins? What theory so far advanced explains the formation of *methane*, and of *that alone*, of the aliphatic hydrocarbons, and its presence in such great quantity? What hypothesis makes clear why substances apparently so widely different as coal and petroleum, olefins and paraffins, acetylenes and the aromatic hydrocarbons, should all yield the same products, or can tell us just why those products and no others should be formed in each case?

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[1] Bull. Soc. Chim. [1], 7, 217.

To the author it seems that these problems have not yet been solved—that the "pyrogenic" reactions, simple or complex as they may be, have never yet been explained, and it is to be hoped that further investigation of this important subject may assist in giving a clearer conception of these peculiar reactions.

In conclusion, the author desires to express his sincere thanks to Dr. A. W. Burwell, not only for the use of his private laboratory, which he so generously placed at my disposal, but also for his constant and valuable aid during the course of the investigation.

Contributions from the Chemical Laboratory of Cornell University.

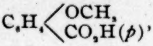
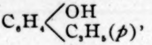
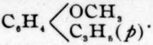
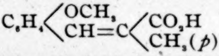
ANETHOL AND ITS ISOMERS.

BY W. R. ORNDORFF, G. L. TERRASSE, AND D. A. MORTON.

Few substances among the compounds of carbon are known in more isomeric modifications than anethol, the chief constituent of the well known oil of anise. No less than nine of these isomers have already been made and described. The names of these are as follows: (1) methyl ether of orthopropenylphenol, (2) methyl ether of metapropenylphenol, (3) methyl ether of chavicol, (4) estragol, (5) fluid metanethol, (6) anisoïn, (7) solid metanethol, (8) isoanethol, and (9) photoanethol.

Comparatively little is known concerning the relation of these substances to each other or to anethol, and in most cases not even the molecular weight has been determined. We have therefore undertaken the study of some of these substances in the hope that we might be able to throw some light on this complicated chapter of the science. Before giving the experimental work, it will be well briefly to review the literature of the subject so that the present state of our knowledge may be clear.

Anethol.

Anethol itself was first carefully studied by Cahours,[1] who showed that it had the formula $C_{10}H_{12}O$, and gave anisic acid,  $C_6H_4\left\langle\begin{matrix}OCH_3\\CO_2H\,(p)\end{matrix}\right.$, and acetic acid on oxidation. Ladenburg and Leverkus[1] then found that with hydriodic acid anethol gave methyl iodide, while on fusion with potassium hydroxide paraanol,  $C_6H_4\left\langle\begin{matrix}OH\\C_3H_5\,(p)\end{matrix}\right.$, together with some paroxybenzoic acid, $C_6H_4\left\langle\begin{matrix}OH\\CO_2H\,(p)\end{matrix}\right.$, resulted. With bromine it very readily formed a dibrom addition-product, $C_{10}H_{12}Br_2O$, and all attempts to replace the oxygen atom in anethol by two atoms of chlorine, by treatment with phosphorus pentachloride, failed. This work with that of Cahours shows that the formula of anethol is  $C_6H_4\left\langle\begin{matrix}OCH_3\\C_3H_5\,(p)\end{matrix}\right.$. The structure of the C_3H_5 group was then determined by Perkin,[2] who made anethol synthetically by heating paramethoxyphenylcrotonic acid,  $C_6H_4\left\langle\begin{matrix}OCH_3\\CH{=}C\left\langle\begin{matrix}CO_2H\\CH_3\,(p)\end{matrix}\right.\end{matrix}\right.$, to its boiling-point, and also by treating the hydrobromic acid addition-product of this acid with a solution of sodium carbonate. Anethol must hence have the following structural formula :

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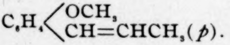
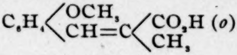
[1] Ann. chim. phys. [3], **2**, 274; **14**, 489.



$$C_6H_4\left\langle\begin{matrix}OCH_3\\CH{=}CHCH_3\,(p)\end{matrix}\right..$$

Anethol is described as an oil with a pleasant odor of anise, crystallizing in plates, which melt at 21.1° C., and boiling at 233° to 233°.5 C. at 751.1 mm. Specific gravity 0.98556 at 21°.6 C. as compared with water at 4° C.

Methyl Ether of Orthopropenylphenol.

This isomer of anethol was made by Perkin[3] by treating the hydriodic acid addition-product of either the α- or the β-orthomethoxyphenylcrotonic acid,  $C_6H_4\left\langle\begin{matrix}OCH_3\\CH{=}C\left\langle\begin{matrix}CO_2H\,(o)\\CH_3\end{matrix}\right.\end{matrix}\right.$, with a solution of sodium carbonate. It is a liquid boiling at 222°–223° C., and having a specific gravity of 0.989, at 30° C.

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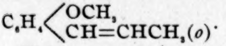
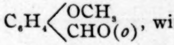
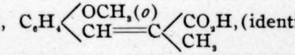
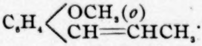
[1] Ann. Chem. (Liebig), Supl. Bd., **8**, 88, and **141**, 260.

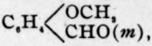
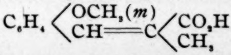
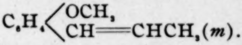
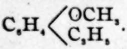
[2] J. Chem. Soc., **31**, 412 ; **33**, 211 ; **39**, 445. See also in this connection Moureu and Chauvet, Bull. Soc. Chim. (Paris), [3], **17**, 411.

[3] J. Chem. Soc., **33**, 213 : **39**, 434.

From its method of formation it must have the formula  $C_6H_4<\begin{matrix}OCH_3\\CH=CHCH_3(o)\end{matrix}$.

This same ether was made by C. Mouren[1] by heating the methyl ether of salicylic aldehyde,  $C_6H_4<\begin{matrix}OCH_3\\CHO(o)\end{matrix}$, with propionic anhydride and fused sodium propionate. Methyl-*o*-propiocumaric acid,  $C_6H_4<\begin{matrix}OCH_3(o)\\CH=C<\begin{matrix}CO_2H\\CH_3\end{matrix}\end{matrix}$, (identical with Perkin's α-methyl-*o*-oxyphenylcrotonic acid), is first formed, and this by the loss of carbon dioxide forms the compound  $C_6H_4<\begin{matrix}OCH_3(o)\\CH=CHCH_3\end{matrix}$. This product is described by Mouren as a liquid boiling at 220°–223° C. at normal pressure, having an odor resembling veratrol, specific gravity of 1.0075 at 0° C., and which does not solidify at —23° C. It readily absorbs one molecule of bromine. From this description of its properties and the mode of formation, there can be no doubt of the identity of the two products. Mouren calls this product orthoanethol.

Methyl Ether of Metapropenylphenol.

This product was also made by C. Mouren, using the methyl ether of methoxybenzoic aldehyde,  $C_6H_4<\begin{matrix}OCH_3\\CHO(m)\end{matrix}$, and heating with propionic anhydride and fused sodium propionate. A similar reaction takes place here as in the case of the formation of the ortho ether of propenylphenol. Methyl-(*m*)-propiocumaric acid,  $C_6H_4<\begin{matrix}OCH_3(m)\\CH=C<\begin{matrix}CO_2H\\CH_3\end{matrix}\end{matrix}$, is first formed, and this by the loss of carbon dioxide, gives the methyl ether of metapropenylphenol,  $C_6H_4<\begin{matrix}OCH_3\\CH=CHCH_3(m)\end{matrix}$. This method of formation fixes the structure of the compound to which Mouren gives the name metaanethol. It is a liquid distilling at 226°–229° C. (uncorr.) at ordinary pressures, and having an odor recalling that of elenic resin. Its specific gravity at 0° is given as 1.0013. It remains liquid when cooled to 23° C., and in chloroform solution at 0° absorbs readily one molecule of bromine. Neither the ortho nor the metaanethol has as yet been found in nature. Mouren made no determinations of the molecular weight of these ethers of propenylphenol, but it is very probable from the mode of formation that they are correctly represented by the formula  $C_6H_4\Big\langle\begin{matrix}OCH_3\\C_3H_5\end{matrix}$.

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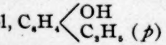
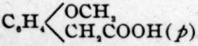
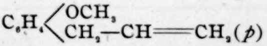
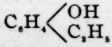
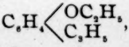
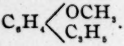
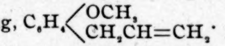
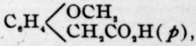
[1] Compt. rend., **123**, 157; Bull. Soc. Chim. (Paris), [3], **15**, 1021.

Methyl Ether of Chavicol.

This substance was made by Eykman[1] in 1888 from chavicol,  $C_6H_4\Big\langle\begin{matrix}OH\\C_3H_5\ (p)\end{matrix}$, which he obtained from Bette leaves. It closely resembles anethol in boiling-point (226° C.), and in other physical properties, though it does not solidify even at $-25°$ C. It has the odor and taste of anise, but weaker than in anethol. It is converted into anethol on boiling with a solution of alcoholic caustic potash, and on oxidation it gives anisic and paramethoxyphenylacetic acid,  $C_6H_4\Big\langle\begin{matrix}OCH_3\\CH_2COOH(p)\end{matrix}$. From these facts Eykman regards methylchavicol as containing the normal allyl grouping and having the formula,  $C_6H_4\Big\langle\begin{matrix}OCH_3\\CH_2-CH=CH_2(p)\end{matrix}$. He finds a further confirmation of this formula in a comparison of the optical constants of methyl chavicol with those of anethol and by a comparison of these constants with those of other compounds known to contain an allyl and a propenyl grouping. Eykman determined the molecular weights of chavicol and of ethylchavicol by the vapor-density method, as well as by the freezing-point method, and found that they agreed with the formulas  $C_6H_4\Big\langle\begin{matrix}OH\\C_3H_5\end{matrix}$ and  $C_6H_4\Big\langle\begin{matrix}OC_2H_5\\C_3H_5\end{matrix}$, respectively, so that it is highly probable that the methyl ether of chavicol has the formula  $C_6H_4\Big\langle\begin{matrix}OCH_3\\C_3H_5\end{matrix}$.

Estragol.

Estragol was first made by Grimaux[2] in 1894 from estragon oil by repeated fractional distillation. He gives the boiling-point 215°–216° C. (corr.), and as this differs from the boiling-point of anethol by about 16°—the usual difference in boiling-point of compounds known to contain the allyl and propenyl grouping, (eugenol and isoeugenol, safrol and isosafrol, apiol and isoapiol),—he is inclined to regard estragol as containing the normal allyl grouping,  $C_6H_4\left\langle\begin{matrix}OCH_3\\CH_2CH=CH_2\end{matrix}\right.$. Like methyl chavicol, it is converted into anethol on heating with an alcoholic solution of potassium hydroxide, and does not solidify at a temperature of — 43° C. Methyl chavicol, Grimaux thinks, may be a stereoisomer of anethol, though he adduces no reason for this view, nor does he state whether he regards it as a cis or a trans compound. He did not determine the molecular weight of estragol, so that we do not know whether it is a metamer or a polymer of anethol. In 1892, some two years before this work of Grimaux on estragol, Schimmel and Co.[1] found that the chief constituent of estragon oil was methylchavicol, and recently their chemists, Bertram and Walbaum,[2] estimated the amount of this substance in estragon oil by Zeisel's method to be 67.8 per cent., and found that by careful oxidation paramethoxyphenylacetic acid,  $C_6H_4\left\langle\begin{matrix}OCH_3\\CH_2CO_2H(p)\end{matrix}\right.$, resulted. This is the same acid that Eykman obtained by oxidizing methylchavicol. It seems highly probable, therefore, that methylchavicol and estragol are identical. This conclusion receives further confirmation from the work of Hell and Gaab,[3] who found that the methylchavicol from estragon oil, (*isoanethol*, they call it), gave a monobrom dibromide, $C_6H_3Br(OCH_3)CH_2CHBrCH_2Br$, when treated with bromine, which on oxidation yielded a ketone having the formula $C_6H_3Br(OCH_3)COCHBrCH_2Br$.

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[1] Ber. d. chem. Ges., **22**, 2736; **23**, 859.

[2] Bull. Soc. chim. (Paris), [3], **11**, 35.

Fluid Metanethol.[4]

This substance was first prepared in 1845 by Gerhardt, and again in 1863 by Kraut and Schlun by distilling anisoïn. It is a liquid with an odor resembling that of the oil of anise, and boiling at 232°.5 C., according to Kraut and Schlun. From the analyses and vapor-density determinations of the product made by him, which boiled at 206° C., Gerhardt concludes that the substance has the formula $C_{10}H_{12}O$, and is therefore a metamer of anethol. According to Kraut and Schlun, it is converted into anisoïn by the action of sulphuric acid, and into isoanethol by heating in sealed tubes to 320° C. for several hours.

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[1] Schimmel and Co.'s Bericht, 1892, 17; see also Hell, J. prakt. Chem. N. F., **51**, 424.

[2] Arch. d. Pharm., **235**, 177, (1897).

[3] Ber. d. chem. Ges., **29**, 344.

[4] J. prakt. Chem., **36**, 272; Arch. d. Pharm. (2), **116**, 241.

Anisoïn.[1]

Passing now to the substances which are probably polymers of anethol, we have first anisoïn, a resinous product made by the action of various polymerizing agents, such as sulphuric and phosphoric acids, tin and antimony chlorides, iodine and benzoyl chloride, on anethol. It is described as a white resinous solid, melting at 140°–145° C., and soluble in concentrated sulphuric acid, forming a beautiful red-colored solution, from which it is reprecipitated unchanged by the addition of water. It is said to crystallize from ether in small needles. It is unaffected by boiling with dilute acids or alkalies, and on distillation it is converted into fluid metanethol and isoanethol. No determinations of its molecular weight have as yet been recorded.

Solid Metanethol.[2]

This substance was first made in 1845 by Gerhardt, by distilling the oil of anise with tin chloride. It was more carefully studied by Perrenoud in 1877. This chemist made the product by the action of fused zinc chloride on anethol. Combustion analyses show that it is an isomer of anethol, but attempts to determine its vapor-density gave unsatisfactory results. It is described as a white, crystalline substance, melting at 132° C., and subliming slowly at 115°–120° C., not volatile with steam, and boiling above 300° C. with decomposition. The molecular weight of this isomer of anethol is also unknown.

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[1] Ann. Chim. phys. [3], **2**, 284; J. prakt. Chem., **36**, 267; Ann. Chem. (Liebig), **65**, 230: J. prakt. Chem., **77**, 490; Arch. d. Pharm. [2], **116**, 241.

[2] J. prakt. Chem., **36**, 272; Ann. Chem. (Liebig), **187**, 68.

Isoanethol.[1]

Isoanethol was prepared by Kraut and Schlun by distilling anisoïn, and also by heating fluid metanethol in sealed tubes at 330° C. for several hours. It is a pale yellow oil, resembling Venice turpentine in consistency. It is said to be stable at 380° C., is unacted on by alcoholic caustic potash solution, but is apparently partially transformed into fluid metanethol by fusion with potassium hydroxide. Both hydriodic and sulphuric acids transform it into anisoïn. Its molecular weight is unknown.

Photoanethol.[2]

This is the name given by Varda to an isomer prepared by him from anethol by the action of sunlight. It is a white, crystalline solid, melting at 207°, tasteless, odorless, non-volatile with steam, but capable of being sublimed. The work of Varda has never been confirmed, nor have any molecular weight determinations of this isomer ever been made.

Experimental.

The anethol used was a very pure specimen, purchased from Fritzsche Bros., of New York City, members of the firm of Schimmel & Co., of Leipzig. It distilled constantly within one degree (232°–233° C. uncorr.), and melted sharply at 21°-22° C. The following analysis shows the product to be very pure :

0.3793 gram anethol gave 0.3102 gram H_2O, and 1.1250 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.10
O	10.81	11.01

Molecular weight determinations, using the boiling-point method and the apparatus devised by Orndorff and Cameron,[3] gave the following results :

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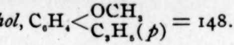
[1] Arch. d. Pharm. (2), **116**, 241.

[2] Gazz. chim. ital., **21**, 183.

[3] This JOURNAL, **17**, 517.

Anethol, 

$C_6H_4 < \begin{matrix} OCH_3 \\ C_3H_5(p) \end{matrix} = 148.$

Solvent, *toluene.* Molecular elevation for 100 grams solvent, 35°.1.

I.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
99.11	0.7053	0.161°	155
"	1.4246	0.289	175
"	2.0868	0.429	172
"	2.7790	0.571	172
"	3.3936	0.720	167
"	4.0585	0.856	168

Barometer, 740.1–740.3. Average, **168**

II.

Grams solvent.	Grams. substance.	Observed elevation.	Molecular weight found.
100	0.6725	0.148°	159.5
"	1.3889	0.309	158
"	1.8677	0.403	162.5
"	2.5862	0.538	169
"	3.3234	0.718	162.4

Barometer constant. Average, **162**

These results, though somewhat high, show conclusively that the molecular weight of anethol is 148, and not 296, or any higher multiple of 148, a result in accord with the vapor-density determinations. In making molecular weight determinations with liquids like anethol and some of the other products described in this paper, we introduced the liquid substance into the boiling-point apparatus in a small bulb having very thin walls (similar to those used in making combustion analyses of liquids). The condenser tube of the apparatus was narrowed a trifle (by softening it in the blowpipe flame and drawing it out a little), below the point where the solvent condensed and ran back into the flask. When the small bulbs were therefore dropped into the upper part of this condenser tube they slid down to this narrow part of the tube and either broke at once or remained there, and were broken by means of a glass rod. The bulbs were filled by means of a capillary pipette, arranged like a medicine dropper. Six or eight of these bulbs could be filled and weighed at the same time, and then be introduced into the apparatus one at a time. This method of introducing liquids into the apparatus has many advantages over the method recommended by Beckmann, not the least of which is that it is very much more accurate, as well as more convenient.

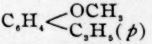
Methyl Chavicol or Estragol.

This substance was prepared from a very excellent specimen of estragon oil, purchased from Fritzsche Bros. The oil was fractionally distilled, using a short Hempel distilling-tube. A good yield of estragol, boiling constantly between 210°–212° C. (uncorr.), was thus obtained, which combustion analyses showed to be a pure product. The following are the results of the analysis:

0.3935 gram estragol gave 0.2903 gram H_2O, and 1.1702 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	81.10
H	8.11	8.20
O	10.81	10.70

Molecular weight determinations by the boiling-point method, using the same apparatus and method of introducing the fluid substance as detailed under anethol, gave the following results:

Methyl Chavicol,  = 148.

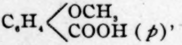
$$C_6H_4<\begin{matrix}OCH_3\\C_3H_5(p)\end{matrix} = 148.$$

Solvent, *toluene.* Molecular elevation, 35°.1.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
101.20	0.6799	0.137°	172
"	1.4536	0.299	169
"	2.0255	0.410	171
"	2.7414	0.555	171
"	3.3480	0.669	173
"	3.8781	0.784	171

Barometer, 737.9–737.8 mm. Average, **171**

These results show that the methylchavicol (or estragol), from estragon oil, has the same molecular weight as anethol, a result which might have been predicted from the fact that methylchavicol is so readily converted into anethol when heated with an alcoholic solution of caustic potash. This specimen of methylchavicol had the peculiar odor characteristic of estragon oil, and all the other properties ascribed to it by Eykman and Grimaux. It remained liquid when cooled to — 22° C., though a few crystals, which seemed to be anethol, formed on the sides of the test-tube in which the oil was cooled.

On oxidation with potassium bichromate and sulphuric acid by the method given by Ladenburg and Fitz[1] for the preparation of anisic acid from anethol it gave anisic acid,  $C_6H_4\begin{cases}OCH_3\\COOH\ (p)\end{cases}$, though the oxidation took place less readily than in the case of anethol, and the yield of acid was much smaller. When treated with bromine in ether solution at 0° C., it readily took up one molecule of bromine, forming apparently a dibrom addition-product.[2] Hydrobromic acid was formed towards the end of the addition of the bromine, and especially on the addition of more than the one molecule of bromine. This work, together with that of other chemists on methylchavicol from estragon oil, and that made from chavicol itself, establishes the complete identity of these substances.

Fluid Metanethol.

To prepare this substance we used the best known method, namely, the distillation of anisoïn. Seventy grams of anisoïn were subjected to dry distillation in a tubulated retort, using a metal bath at first to get some idea of the temperature, and finally heating with a direct flame. The anisoïn first melts to a yellowish oil, and then slow distillation occurs at 350° C., but a temperature above 400° C. is required for rapid distillation. About sixty-six grams of the crude fluid metanethol were obtained. This was distilled in a current of steam to separate the fluid metanethol from the isoanethol formed in the reaction. The oil distilling with the water was separated,

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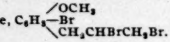
[1] Ann. Chem. (Liebig), **141**, 248.

[2] Hell and Gaab: Ber. d. chem. Ges., **29**, 344, found that it was impossible to isolate the dibromide, but did succeed in obtaining a monobrom isoanethol (methylchavicol) dibromide,  $C_6H_3\begin{cases}OCH_3\\Br\\CH_2CHBrCH_2Br.\end{cases}$

dried with fused calcium chloride, and fractionally distilled through a short Hempel tube. The oil begins to distil at 205° C., the thermometer rising rapidly to 225° C., and then gradually to 230°, above which temperature only a small fraction remained in the flask. The greater bulk of the liquid distilled from 228°–229°, and on redistillation of the fraction 225°–230° nearly all came over between 226°–229° C. (uncor.). Analysis of this product shows that it is pure. The following are the results obtained :

0.4424 gram fluid metanethol gave 0.3305 gram H_2O, and 1.3122 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.30
O	10.81	10.81

Molecular weight determinations by the boiling-point method gave the following results :

Fluid Metanethol, $C_{10}H_{12}O = 148$.

Solvent, *chloroform*. Molecular elevation for 100 grams, 36°.6.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
184.77	0.6013	0.070°	170
"	1.4394	0.170	168
"	2.0221	0.240	167
"	2.6419	0.320	164
"	3.3052	0.400	164

Barometer, 744.7–743.5 mm. Average, 166

These results point to a molecular weight of 148 for fluid metanethol, and show that the substance is a metamer of anethol, a result in accord with the vapor-density determinations made by Gerhardt with the product made by him, but boiling at 206° C.

Fluid metanethol is a perfectly clear, limpid, colorless oil, having an odor resembling that of oil of anise, but quite distinct from that of anethol itself. When cooled in a freezing-mixture of ice and concentrated hydrochloric acid and agitated, it solidifies to a mass of crystals, resembling crystallized anethol very closely. These crystals melt between 4° and 5° C. The freezing-point of the fluid metanethol, carefully determined with the Beckmann apparatus, was found to be 3°.1 C. When boiled with alcoholic caustic potash solution for six hours, fluid metanethol undergoes no change. The specific gravity at 20° C. was found to be 0.9852.

When oxidized with potassium bichromate and sulphuric acid, by the method of Ladenburg and Fitz,[1] it acted exactly like anethol, and gave an abundant yield of anisic acid,

$C_6H_4\left\langle\begin{matrix}OCH_3\\CO_2H\end{matrix}\right.(p)$. When cooled to 0° C. in solution in ether and treated with bromine, it took up readily one molecule of bromine, forming a dibrom addition-product, which resembled the dibrom addition-product of anethol[2] very closely, but which melted at 63° C., and was evidently not identical with anethol dibromide.

The following are the results of the analysis of this product recrystallized from petroleum ether:

0.2094 gram substance gave 0.2543 gram AgBr.

	Calculated for $C_{10}H_{12}OBr_2$.	Found.
Br	51.9	51.7

Attempts to make fluid metanethol by other methods were unsuccessful. A small quantity is formed when anethol is distilled with fused zinc chloride, but the best method is the one given above, by the distillation of anisoïn.

Anisoïn.

Attempts to make anisoïn by the action of hydrochloric acid on anethol, as well as by the action of dilute sulphuric acid, gave unsatisfactory results. The method of Will and Rhodius was then tried and found to give practically a quantitative conversion of the anethol into anisoïn. A saturated solution of iodine in an aqueous solution of potassium iodide was prepared, and into this was slowly dropped 150 grams of pure anethol. Some unknown volatile compound appears to be formed in small quantity, which affects the mucous membranes of the eyes and nose disagreeably. The black resinous mass thus obtained was allowed to stand in contact with the iodine solution for about two hours. After draining off the iodine solution, the mass was pulverized and boiled five times with a dilute solution of potassium iodide in order partially to remove the iodine. The product was then triturated repeatedly with cold alcohol until it had acquired a pale brown hue. It was then dissolved in benzene and precipitated from the filtered solution by the addition of alcohol. It is precipitated from this solution as a gummy mass, and for this reason benzene is not to be recommended for its purification. The whole amount was now dissolved in a small quantity of ethyl acetate, and precipitated with alcohol. This treatment gave 135 grams of a pure white product, or a yield of 90 per cent., and no especial care was taken to collect all the material from the residues.

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[1] Ann. Chem. (Liebig), **141**, 248.

[2] Ladenburg: Ann. Chem. (Liebig), Spl. Bd., **8**, 94; Ber. d. chem. Ges., **2**, 372; see also Wallach: Ber. d. chem. Ges., **28**, 2714, and Hell and Günthert: J. prakt. Chem., **52**, 198.

Anisoïn was also prepared by the sulphuric acid method of Cahours.

Much time and labor were devoted to preparing pure anisoïn, but all attempts to obtain crystals of the product larger than doubtful microscopic ones, failed, although carbon disulphide, benzene, chloroform, ether, ethyl acetate, alcohol and acetone, and several combinations of these solvents were tried. The product was generally obtained when the solvent had completely evaporated, as a horn-like mass showing no evidence of crystallization. By very slowly cooling an aqueous acetone solution of anisoïn, the substance separated in small clear grains, which appeared to be crystalline to the unaided eye, but under the microscope proved to be merely rounded grains showing no crystal faces, and having no action on polarized light. They were therefore either amorphous or isotropic.

The following are the results of the analyses of the various products obtained :

I. Product melting at 181°–184°, made by the iodine method.

0.4074 gram anisoïn gave 0.2899 gram H_2O, and 1.1896 grams CO_2.

II. Product melting at 132°–140°, made by the iodine method.

0.1530 gram anisoïn gave 0.1116 gram H_2O, and 0.4463 gram CO_2.

III.[1] Product melting at 180°–192°, made by the iodine method.

IV. Product melting at 172°–190°, made by the sulphuric acid method.

0.1728 gram anisoïn gave 0.1250 gram H_2O, and 0.4997 gram CO_2.

V. Product melting at 190°–192°, made by the iodine method.

0.1705 gram anisoïn gave 0.1260 gram H_2O, and 0.5038 gram CO_2.

	Calculated for $C_{10}H_{12}O$.	Found. I.	II.	III.	IV.	V.
C	81.08	79.64	79.56	79.81	78.89	80.59
H	8.10	7.91	8.10	8.04	8.04	8.21
O	10.82	12.45	12.44	12.15	13.07	11.20

Products Number I. and II. were slightly yellow, the others were pure white; I. and II. were purified by dissolving in acetic ether and precipitating by the addition of alcohol; III., IV. and V., by precipitating from acetone solution by the addition of water. Molecular weight determinations by the boiling-point method, using acetone, acetic ether, and benzene as solvents, were attempted without satisfactory results.[2] The boiling-points of these solvents remained unchanged even when over a gram of the anisoïn had been introduced. Anisoïn thus appears to be a colloid, and does not form a true solution in these solvents.

Solid Metanethol.

As Perrenoud's method for the preparation of solid metanethol gave only a small yield of the substance, attempts were made to improve the method. As these changes did not accomplish their object, it is not necessary to detail them here.

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[1] The results obtained in this analysis were lost, and only the percentage figures can therefore be given.

[2] The attempts to determine the molecular weight of anisoïn, both by the boiling-point and freezing-point methods, were made by Mr. H. J. Steuber, to whom we wish here to express our thanks.

Working according to Perrenoud's directions, 60 grams of anethol were heated in a retort with 120 grams of freshly fused zinc chloride until white fumes began to appear in the retort, when superheated steam was passed in. The solid material in the distillate was separated from the water, treated with alcohol and ether to remove unattacked anethol and fluid metanethol, and recrystallized from a mixture of absolute alcohol and chloroform, after boiling with bone-black to remove the color from the solution. A pure white product is thus obtained, but the yield is very small—only 4 grams from the 60 of anethol used. Combustion analyses of this product, melting at 123°–125° C., showed that it was not pure. The following are the results obtained:

I. 0.3305 gram solid metanethol gave 0.2362 gram H_2O, and 0.9602 gram CO_2.

II. 0.4119 gram solid metanethol gave 0.2940 gram H_2O, and 1.1976 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found. I.	Found. II.
C	81.08	79.24	79.29
H	8.11	7.94	7.93

The product was further purified by carefully crystallizing from boiling glacial acetic acid. It now melted at 133°–133°.5 and gave the following results on analysis:

0.1922 gram substance gave 0.1422 gram H_2O, and 0.5690 gram CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.75
H	8.11	8.22
O	10.81	11.03

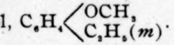
Attempts to determine the molecular weight of solid metanethol by the boiling-point method, using both toluene and chloroform, gave unsatisfactory results, as the substance underwent decomposition in both these solvents. Using the freezing-point method, and benzene as a solvent, the following results were obtained.

Solid Metanethol,[1] $(C_{10}H_{12}O)_2 = 296$.

Solvent, *benzene.*

Grams solvent.	Gram substance.	Observed depression.	Molecular weight found.
24.4264	0.0791	0.065°	244
"	0.1632	0.125	262
12.039	0.1180	0.173	277

These results point to the formula $(C_{10}H_{12}O)_2$ as the formula for solid metanethol. It would be better therefore to call this substance dianethol, and discard the term metanethol, which is confusing, as it is also used for the methyl ether of metapropenylphenol,



$C_6H_4\left\langle\begin{matrix}OCH_3\\C_3H_5(m)\end{matrix}\right.$.

Isoanethol.

This product was made at the same time as the fluid metanethol by the distillation of anisoïn. It was separated from the fluid metanethol by distillation in steam, remaining in the distillation-flask as a heavy viscous oil. An attempt was made to purify it by the method of Kraut and Schlun, but as this proved unsuccessful, it was subjected to fractional distillation under reduced pressure (100 mm.). A product was finally obtained boiling at 245°–255° (at 100 mm. pressure). This was a pale yellow oil of a thick syrupy consistency, which soon acquired a red color on standing. The yield was small and the product is extremely difficult to purify. An analysis gave the following results :

0.4424 gram isoanethol gave 0.3305 gram H_2O, and 1.3122 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.38
O	10.81	11.05

Molecular weight determinations in chloroform solution by the boiling-point method gave the following results :

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[1] These determinations were made for us by Mr. H. J. Steuber, to whom we wish here to express our thanks.

Isoanethol, $(C_{10}H_{12}O)_2 = 296$.

Solvent, *chloroform*. Molecular elevation for 100 grams, 36°.6.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
190.24	0.5350	0.035°	294
"	1.6477	0.100	317
"	2.2620	0.132	330
"	2.8330	0.160	341

Molecular weight at infinite dilution, **280**

Barometer, 746.1–745.9 mm.

Molecular weight determinations in toluene, by the boiling-point method, gave unsatisfactory results owing to the decomposition of the isoanethol in this solvent. Molecular weight determinations by the freezing-point method, using benzene as a solvent, gave the following results :

Isoanethol,[1] $(C_{10}H_{12}O)_2 = 296$.

Solvent, *benzene*.

Grams solvent.	Gram substance.	Observed depression.	Molecular weight found.
10.9630	0.1625	0.275°	264
"	0.3631	0.630	258
12.1770	0.1192	0.195	246
"	0.2625	0.423	248

These results show that isoanethol, like the solid metanethol, has twice the molecular weight of anethol. It would therefore be better to call this substance dianethol, and, to distinguish it from the solid metanethol, it might be called fluid dianethol, while the solid metanethol could be named solid dianethol.

Photoanethol.

Two attempts to make this substance by allowing bottles containing pure anethol to stand in the sunlight for three months, resulted unsatisfactorily. On distillation the whole amount of the liquid distilled at 232°–233° C., and only a very small amount of a tarry residue, too small to be examined, was left in the flask. A third attempt, in which the anethol was exposed for five months during the summer of 1896, gave a small amount of the photoanethol. The product was separated from the anethol by the method given by Varda. It crystallized in leaflets having a mother-of-pearl luster, and melting at 207° C. Unfortunately the amount obtained was too small for further study.

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[1] **These determinations were made for us by Mr. H. J. Steuber, to whom we wish here to express our thanks.**

The Action of Heat on Anethol.

As fluid metanethol results from the distillation of anisoïn, it was thought that anethol might be converted directly into its isomer, fluid metanethol, by the action of heat. Preliminary experiments showed that when anethol is heated in sealed tubes to 275°–290° C., it is completely changed. 300 grams of anethol were then heated in an autoclave for two and a half hours to 250°–275°. The pressure, as shown by the manometer, varied from seven to twelve atmospheres. No free anethol could be detected in the crude product, which had become tarry in appearance and consistency. This tarry mass was distilled in steam. The residue left in the flask, when distilled under reduced pressure, gave isoanethol. The oily distillate was separated from the water, dried and subjected to fractional distillation, a short Hempel distilling tube being used. Two fractions were isolated, one boiling at 174°–178° C., and the other at 209°–212° C.

Analyses of the fraction boiling at 174°–178° C. gave the following results :

I. 0.3477 gram of product gave 0.2576 gram H_2O, and 0.9996 gram CO_2.

II. 0.3663 gram of product gave 0.2707 gram H_2O, and 1.0537 grams CO_2.

	Calculated for $C_8H_{10}O$.	Found. I.	II.
C	78.69	78.40	78.45
H	8.20	8.23	8.21
O	13.11	13.37	13.34

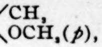
Molecular weight determinations by the boiling-point method gave the following results :

Product boiling at 174°–178° C., $C_8H_{10}O = 120$.

Solvent, *chloroform*.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
189.25	0.9470	0.164°	112
"	1.6137	0.296	106
"	2.2167	0.393	109
"	3.1666	0.554	111
"	3.8178	0.670	110

Barometer, 735.1–735.5 mm. Average, 110

These results show that the compound has the formula $C_8H_{10}O$. A comparison of the properties of this product with those of the methyl ether of paracresol, C_6H_4  $C_6H_4<\begin{matrix}CH_3\\OCH_3(p)\end{matrix}$, shows that the two substances are identical.

A combustion analysis of the product boiling at 209°–212° C., gave the following results:

0.3772 gram product gave 0.3142 gram H_2O, and 1.1020 grams CO_2.

	Calculated for $C_{10}H_{14}O$.	Found.
C	80.00	79.68
H	9.33	9.26
O	10.67	11.06

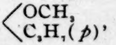
Molecular weight determinations by the boiling-point method gave the following results:

Product boiling at 209°–212° C., $C_{10}H_{14}O = 150$.

Solvent, *toluene*.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
106.72	0.6996	0.137°	168
"	1.5684	0.305	169
"	2.1653	0.410	173
"	2.9004	0.548	174
"	3.7063	0.708	172

Barometer, 741.3–740.6 mm. Average, 171

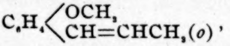
These results show that the product has the formula $C_{10}H_{14}O$. It was found to correspond in all its properties to the methyl ether of parapropylphenol, C_6H_4  $C_6H_4<\begin{matrix}OCH_3\\C_3H_7(p)\end{matrix}$, but whether it contained the normal or the isopropyl group could not be determined, though from its method of formation from anethol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ CH=CHCH_3(p)\end{matrix}\right.$, it is probable that it contains normal propyl.

Anethol was found to undergo the same change when boiled for a long time in a flask connected with a return condenser. It is possible that had the fractionation been conducted differently the methyl ether of paraethylphenol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ C_2H_5(p)\end{matrix}\right.$, would also have been isolated from the product of the action of heat on anethol.

Theoretical.

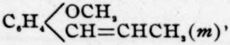
A substance having the formula $C_6H_4\left\langle\begin{matrix}OCH_3\\ C_3H_5\end{matrix}\right.$ may exist in no less than fifteen metameric modifications, as follows:

1^1-Propenylphenol-(2)-methyl ether or orthoanethol,



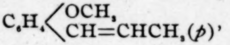
$$C_6H_4\left\langle\begin{matrix}OCH_3\\ CH=CHCH_3(o)\end{matrix}\right.,$$

1^1-Propenylphenol-(3)-methyl ether or metaanethol,



$$C_6H_4\left\langle\begin{matrix}OCH_3\\ CH=CHCH_3(m)\end{matrix}\right.,$$

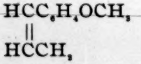
1^1-Propenylphenol-(4)-methyl ether or paraanethol,



$$C_6H_4\left\langle\begin{matrix}OCH_3\\ CH=CHCH_3(p)\end{matrix}\right.,$$

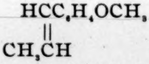
the last being generally known simply as anethol.

Each of these substances could exist in two stereoisomeric modifications, the one cis, the other trans are shown in the following formulas:



$$\begin{array}{l}HCC_6H_4OCH_3\\ \quad\|\\ HCCH_3\end{array}$$

Cis-propenylphenol methyl ether.

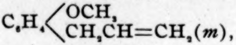


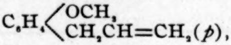
$$\begin{array}{l}\;\;HCC_6H_4OCH_3\\ \qquad\|\\ CH_3CH\end{array}$$

Transpropenylphenol methyl ether.

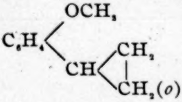
Six propenylphenol methyl ethers of the above formulas are therefore possible.

1^2-Propenylphenol-(2)-methyl ether or orthoallylphenol methyl ether, $C_6H_4\left\langle\begin{matrix}OCH_3\\ CH_2CH=CH_2(o)\end{matrix}\right.$,

1^2-Propenylphenol-(3)-methyl ether or metaallylphenol methyl ether,  $C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH_2CH=CH_2(m)\end{matrix}$,

1^2-Propenylphenol-(4)-methyl ether or paraallylphenol methyl ether,  $C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH_2CH=CH_2(p)\end{matrix}$,
are also all possible theoretically, making nine isomers.

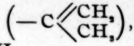
Then we may have three more isomers, ortho, meta and para, having the following structural formula,

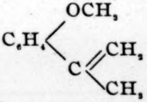


$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH\begin{matrix}\diagup CH_2\\ |\\ \diagdown CH_2\end{matrix}\end{matrix}$

(o), (m), (p), which might be called

1-Cyclopropenylphenol-(2), (3) and (4) methyl ether.

Finally we may have three isomers, ortho, meta and para containing the so-called isoallyl grouping  $\left(-C\begin{matrix}\diagup\!\!\diagup CH_2\\ \diagdown CH_3\end{matrix}\right)$, and having the structural formula

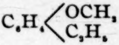


$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C\begin{matrix}\diagup\!\!\diagup CH_2\\ \diagdown CH_3\end{matrix}\end{matrix}$

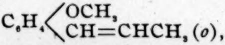
(o), (m), (p).

These might be named

1-Methoethenylphenol-(2), (3) and (4)-methyl ether or ortho, meta and para isoallylphenol methyl ether.

Five substances having the formula  $C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C_3H_5\end{matrix}$ are now known. These are:

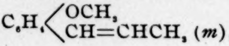
1^1-Propenylphenol-(2)-methyl ether or orthoanethol,



$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH=CHCH_3\,(o)\end{matrix}$,

made by Perkin, and later by Mouren;

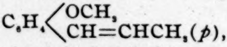
1^1-Propenylphenol-(3)-methyl ether or metaanethol,



$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH=CHCH_3\,(m)\end{matrix}$,

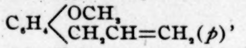
made by Mouren;

1^1-Propenylphenol-(4)-methyl ether or paraanethol,

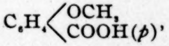


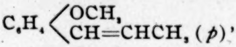
$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH=CHCH_3(p)\end{matrix}$,

generally known simply as anethol;

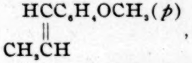
1^3-Propenylphenol-(4)-methyl ether or paraallylphenol methyl ether  $C_6H_4\begin{cases}OCH_3\\CH_2CH{=}CH_2(p)\end{cases}$, called the methyl ether of chavicol by Eykman, estragol by Grimaux, and isoanethol by Hell and Gaab, and finally the substance known as fluid metanethol.

Regarding the first four of these substances the evidence upon which the above formulas are based must be considered conclusive.

The last substance, fluid metanethol, we regard as a stereoisomer of 1^1-propenylphenol-(4)-methyl ether, or ordinary anethol, for the following reasons: First, the analyses and molecular weight determinations show conclusively that its composition is correctly represented by the formula $C_{10}H_{12}O$; secondly, it gives anisic acid on oxidation, and as this substance undoubtedly has the formula  $C_6H_4\begin{cases}OCH_3\\COOH(p)\end{cases}$, fluid metanethol must be a para compound, and must contain the methoxy group, $(-OCH_3)$, as well as the group, $(-C_3H_5)$; thirdly, it gives with bromine very readily a dibrom addition-product, which resembles closely, but yet is different from that obtained from anethol, hence the group C_3H_5 is unsaturated and contains one double bond; fourthly, fluid metanethol undergoes no change on boiling with an alcoholic solution of caustic potash, and hence does not contain the normal allyl grouping $-CH_2-CH{=}CH_2$, as all compounds known to contain this grouping are changed into propenyl compounds containing the group $-CH{=}CHCH_3$ by this treatment. This conclusion is further justified by the fact that fluid metanethol has a higher boiling-point and melting-point than the methyl ether of paraallylphenol (estragol, methyl chavicol), substances containing the propenyl grouping invariably boiling and melting at higher temperatures than the corresponding allyl compounds. In connection with this conclusion it is perhaps well to mention here that the methyl ether of paraallylphenol (methyl chavicol, estragol), is converted into 1^1-propenylphenol-(4)-methyl ether (ordinary anethol,) on boiling with a solution of caustic potash in alcohol.

For these reasons the formula of the fluid metanethol must be  $C_6H_4\begin{cases}OCH_3\\CH{=}CHCH_3\ (p)\end{cases}$, and it would be better to call the substance 1¹-propenylphenol-(4)-methyl ether, and discard the name fluid metanethol, which is old and misleading, now that the substance has been shown to be a para compound, and Mouren has made a substance which is really a metanethol. This formula is further in accord with the formation of the substance from anethol by distilling with fused zinc chloride, and by distilling the anisoïn resulting from the polymerization of anethol.

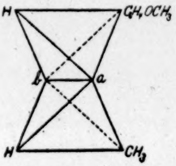
Regarding the further question as to which of these two compounds corresponds to the cis configuration and which to the trans, we are inclined to regard fluid metanethol as the trans compound,



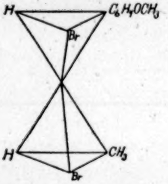
$$\begin{array}{l}HCC_6H_4OCH_3(p)\\ \quad\ \ \|\\ CH_3CH\end{array},$$

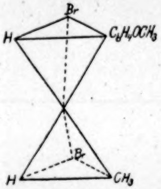
as it is formed at a high temperature, and is evidently the more stable modification at high temperatures. Further work will be necessary, however, to test this point. Assuming that it is the trans compound, it would be called trans-1¹-propenylphenol-(4)-methyl ether, while ordinary anethol would be cis-1¹-propenylphenol-(4)-methyl ether. If it be thought desirable to use shorter names, we might call fluid metanethol trans-paranethol, and ordinary anethol cis-paranethol.

The formation of two different dibrom addition-products, one from the cis- and the other from the trans-anethol is in perfect accord with these formulas. For assuming the cis formula for ordinary anethol,



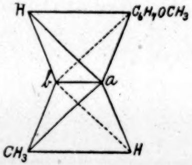
it will be seen that when bromine is added either at *a* or *b* two compounds will be formed. These are right and left



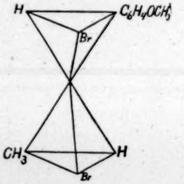


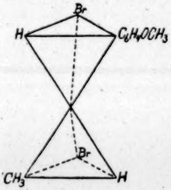
structures or enantiomorphous forms, and as both would be formed in equal amount, the product would be the inactive or racemoid type of the cisanetholdibromide.

When bromine is added to the trans compound, two dibro-



mides will also be formed, one a right and the other a left, as shown in the formulas:

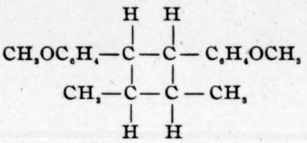




Both these substances will be formed in equal amount, and hence the product would be the racemoid type of the transanetholdibromide. It will be seen by a careful comparison of these formulas that the dibromides from cis-anethol and transanethol, though they should resemble each other closely, should nevertheless be different, as they are in fact, as has been shown in the experimental part of this work.

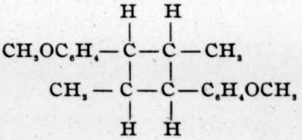
In the naming of anethol and its isomers, the method has been haphazard and bad, and the result is much confusion. The "ol" termination ought not to be used, as the substance is neither an alcohol nor a phenol. Hence such names as ortho, met- and paranethol should be discarded. Such names as ortho, meta and parapropenylanisol, which have been proposed for (*o*), (*m*) and (*p*) anethol, are also bad, first because of the "ol" termination, and secondly, because the kind of group is not sufficiently determined by the use of the word propenyl. Such names as anethoïl and anisoïl have also but little to recommend them. In this article we have, therefore, so far as possible, given the substances names in accord with the recommendations of the Geneva Conference of Chemists. These are long and cumbersome, but accurate and definite, and therefore to be preferred.

Concerning the structure of the two polymers of anethol, called isoanethol and solid metanethol, which we have shown to have twice the molecular weight of anethol, and to be really dianethols, we can say very little. Both substances seem to act like saturated compounds, so that they may be represented by formulae like these :

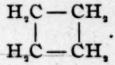


$$\begin{array}{rcccl} & H & & H & \\ & | & & | & \\ CH_3OC_6H_4- & C & - & C & -C_6H_4OCH_3 \\ & | & & | & \\ CH_3- & C & - & C & -CH_3 \\ & | & & | & \\ & H & & H & \end{array}$$

and



$$\begin{array}{rcccl} & H & & H & \\ & | & & | & \\ CH_3OC_6H_4- & C & - & C & -CH_3 \\ & | & & | & \\ CH_3- & C & - & C & -C_6H_4OCH_3 \\ & | & & | & \\ & H & & H & \end{array}$$

and may be derivatives of tetramethylene,  $\begin{array}{ccc} H_2C & - & CH_2 \\ | & & | \\ H_2C & - & CH_2 \end{array}$.

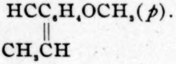
Regarding anisoïn we can only say that the molecular weight determinations in benzene, acetic ether, and acetone show that the substance does not form a true solution in these solvents.

Summary.

The results of this work on anethol and its isomers may be summed up as follows:

1. Methylchavicol of Eykman, and estragol of Grimaux, have the same molecular weight, and are metamers of anethol. From the work done on the two substances by different chemists, we must conclude that they are identical.

2. Fluid metanethol also has the same molecular weight as anethol, and is a metamer of this substance. From its chemical conduct, in which it resembles anethol very closely, and physical properties, it must be regarded as a stereoisomer of anethol, and is probably the trans compound



$$\begin{array}{l}HCC_6H_4OCH_3(p).\\ \;\;\,\|\\ CH_3CH\end{array}$$

3. Anisoïn, the resinous polymeric modification of anethol, acts as a colloid towards the solvents, acetic ether, acetone, and benzene.

4. Solid metanethol and the liquid isoanethol both have the same molecular weight and are polymers of anethol. As their molecular weight is twice that of anethol, they should be called solid dianethol and fluid dianethol respectively. As they both act like saturated compounds, it is possible that they are derivatives of tetramethylene.

5. Names have been suggested for anethol and its isomers, which are in accord with the suggestions of the Geneva Conference of Chemists, and are more in accord with the present state of our knowledge on the subject.

6. By heating anethol under pressure to 250°–275°, it is transformed into isoanethol, the methyl ether of paracresol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ CH_3(p)\end{matrix}\right.$, and the methyl ether of parapropylphenol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ C_3H_7(p)\end{matrix}\right.$, the tendency under these conditions being apparently to form saturated compounds.

Further work on these substances, especially on the so-called fluid metanethol, will be undertaken in this laboratory.

CORNELL UNIVERSITY,
JUNE, 1897.

ACTION OF SULPHUR ON SILICIDES. PRODUCTION OF SILICON.

BY G. DE CHALMOT.

Action of Sulphur on Copper Silicide.

In a former article[1] I have shown that an alloy of free copper, free crystalline silicon, and copper silicide, Cu_2Si, can be obtained if silica is reduced in the presence of copper and at a very high temperature. If this alloy is treated with boiling diluted nitric acid, or with aqua regia, etc., all the copper can be dissolved and the silicon of the copper silicide will be oxidized to silica, while the free crystalline silicon remains unaltered. Hydrofluoric acid dissolves the silica, and silicon remains. This method of obtaining free silicon would be much more efficient if a large part of the silicon did not combine with the copper, being thus lost in the solutions. That this loss is quite considerable is shown by the following figures, which were obtained by the analysis of a copper silicide of average quality :

	Per cent.
Total copper	70.05
Iron	0.87
Free silicon	19.21
Combined silicon	10.10

I have tried to find a substance that will combine with the copper and react with the silicide in such a manner that the silicon is liberated according to the formula :

$$Cu_2Si + X = Cu_2X + Si.$$

I have partially succeeded in this by using sulphur. It is well known that copper and sulphur have a great affinity for each other, and that copper will even extract sulphur from iron sulphide at a temperature far below the melting-point of either substance.[2]

According to Berzelius, amorphous silicon and sulphur also react at a rather low temperature, and the reaction is even quite violent at a high temperature.

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[1] This JOURNAL, 19, 118.

[2] Colson : Compt. rend., 93, 74.

That sulphur would attack the copper silicide at a not too elevated temperature was likely, since copper and silicon have no great affinity for each other, a fact that is evident from the non-existence of a compound $CuSi_2$, and also from the fact that even the compound Cu_2Si will dissociate at very high temperatures, while no such reaction is known in the case of other silicides. In my experiments I mixed the well pulverized alloys with sulphur and heated them in a drying-box in closed glass tubes.

The sulphur commences to be absorbed between 200°–250° C., but the reaction is very slow. It can be completed at 270°–280° C. If the temperature is elevated much above 300° C. the reaction $Si + S_2 = SiS_2$ is much facilitated and this is detrimental to the result.

In some cases I have added just sufficient sulphur for all the copper to form cuprous sulphide, Cu_2S ; in other cases I have added about twice as much, so that cupric sulphide, CuS, could be formed. In both instances, all or almost all the sulphur was absorbed, while much amorphous silicon had been liberated. The amount liberated was, however, less when more sulphur was taken. It appears that at the temperature mentioned the conditions favor the reactions :

$$2Cu + S = Cu_2S, \quad \text{and}$$
$$Cu_2S + S = 2CuS,$$

in preference to the reaction

$$Si + 2S = SiS_2.$$

In all cases, however, the reaction was not only between the copper and the sulphur. The odor of hydrogen sulphide that was given off when the product was ground up showed that some silicon and sulphur had combined, because the presence of the hydrogen sulphide can only be explained by the decomposition of the compound SiS_2 by the moisture of the air. In fact the analysis showed that only one-half to two-thirds of the combined silicon had been liberated or at least withstood the attack of the solvent liquids.

The sulphur in the mixtures, heated above its melting-point, would run together into little drops, causing a local excess of sulphur at many places, which, of course, favored the formation of silicon sulphide. I showed that this compound was formed to a considerable extent by heating the ground product with water and absorbing the hydrogen sulphide that was given off. The hydrogen sulphide was precipitated with sodium arsenate.

It is, therefore, not alone due to the action of the solvents to which the silicon is afterwards subjected that the yield is not the theoretical. In how far these solvents affect this amorphous silicon I do not know, but judging from my results and those of Vigoureux,[1] I should say that neither boiling diluted nitric acid nor hydrofluoric acid attack it to any great extent. The product obtained in the glass tube was ground up and well mixed, and a portion was used for determining the percentage of free silicon in the product. By taking into account the amount of sulphur that had been added, and the composition of the original alloy, the gain in free silicon could be calculated. In some cases sulphur would remain uncombined and stick to the sides of the tube. Its weight was taken into account, being found by dissolving sulphur in carbon disulphide. The sample taken for analysis, 1–2 grams, was treating with boiling diluted nitric acid. The residue was filtered from the copper solution, the filter and contents were dried, and the sulphur that is formed from the copper sulphide was extracted with carbon disulphide. The residue from this treatment was now carefully scraped from the filter and put into one platinum dish and the filter was cut into small pieces and put in another. Cold, strong, hydrofluoric acid was allowed to act on both filter and residue for twenty-four hours. The contents of both dishes were then filtered. The cut-up filter was washed free of acid without being brought on the filter, the washings being filtered, of course. The whole of the contents and all the filter-paper was brought in a porcelain crucible and dried, and the paper burnt, when the contents and ashes were mixed with soda potash and some saltpeter, and the insoluble silicon determined as usual. In the residue iron and copper were also determined, and their presence explained by the presence of silicides, $FeSi_2$ and Cu_2Si, and the amount of silicon required to form these compounds was deducted from the insoluble silicon to find the free silicon. There were only traces of iron and but little more copper.

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[1] Compt. rend., **120**, 369.

It was somewhat arbitrary to explain the presence of copper by assuming the presence of copper silicide. In fact, when the hydrofluoric acid acted on the residue the odor of hydrogen sulphide was quite perceptible. It is, therefore, probable that the copper was present as sulphide and that the silicon which enveloped it had prevented the nitric acid from attacking it; and that, when the sulphur was removed, the hydrofluoric acid formed the fluoride, which is quite insoluble. In that case the figures given below for free silicon in the products are too low by 0.1–0.2 per cent. There were no sulphates or only traces with the silica obtained by fusing the residue of the treatment with soda.

After having found that a large part of the combined silicon in a high-grade silicon alloy can be liberated, I also tried a low-grade alloy with the same result. In the latter case I could better examine the amorphous silicon as it is mixed with much crystalline silicon if made from high-grade silicides.

Experiment I.

5 grams high-grade silicon alloy was heated with 0.9 gram sulphur. The temperature was never over 290° C.

	Before treatment.	After treatment with sulphur.
	Per cent.	Per cent. of original alloy.
Total silicon	29.31	....
Free "	19.21	25.77
Combined silicon	10.10	3.54
Copper	70.05	....
Iron	0.87	....

Experiment II.

5 grams low-grade silicon alloy were heated with 1.08 grams sulphur. The temperature rose to 320° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	7.84
Combined silicon	11.74	5.12
Copper	86.42	....
Iron	0.84	....

Experiment III.

5 grams of the same low-grade alloy were treated with 2 grams sulphur. The temperature was 310–330° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	6.20
Combined silicon	11.74	6.76

Experiment IV.

5 grams of the same low-grade alloy were treated with 2 grams sulphur. The temperature was kept under at 290° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	7.27
Combined silicon	11.74	5.69

The influence of the temperature becomes evident by comparing Experiments III. and IV. At 310–320° C. the amount of free silicon in the product is one per cent. less than if the temperature was only 290° C. That the larger amount of sulphur is detrimental is plain on comparing Experiments II. and especially I. with Experiments III. and IV.

Action of Sulphur on Manganese Silicide.

Manganese silicide, $MnSi_2$, is much less readily attacked than copper silicide. I have, in fact, found it impossible to obtain free amorphous silicon by heating the same with sulphur. Below 300° C. there is practically no reaction between the silicide and sulphur. I also heated a mixture of these substances in an open glass tube at the boiling-point of sulphur, and in a closed combustion tube, until the latter commenced to swell from the pressure of the sulphur vapor. In these cases I obtained products which gave the odor of hydrogen sulphide when ground up, which shows that some silicon sulphide, SiS_2, had been formed. I heated in a hard glass tube, as described, 1 gram of sulphur and 4 grams of silicide which contained: Manganese, 42.99 per cent.; free silicon, 8.26 per cent.; and an appreciable quantity of iron.

The product which had the odor of hydrogen sulphide was ground up and extracted with carbon disulphide. The residue had much the appearance of the original silicide, and contained a little insoluble sulphur. Boiling dilute nitric acid did not attack it. I therefore treated it at once with cold hydrofluoric acid, which dissolved the larger part, leaving some crystalline silicon and the insoluble sulphur. The analysis showed it to contain:

	Per cent.
Manganese	44.43
Free silicon	7.37

The relation of the amounts of manganese to free silicon before and after treatment with sulphur are as follows:

Before treatment.	After treatment.
Mn : Si = 100 : 19.2	Mn : Si = 100 : 16.6

This shows conclusively that no silicon has been liberated. In fact it appears that at the higher temperature which was required to bring about any action, the sulphur has attacked a part of the crystalline silicon.

Action of Sulphur on Chromium Silicide.

Chromium silicide, $CrSi_2$, is not acted on by sulphur at 300° C. I heated 1.30 grams sulphur with 4 grams silicide which contain 54 per cent. chromium and a trace of free silicon. The materials were well mixed. The mixture was put in a closed glass tube and was heated to 450° C. in a drying oven. There seemed to be some reaction, as all the sulphur was equally absorbed by the silicide. The product had the odor of hydrogen sulphide. When it was treated with carbon disulphide, quantities of sulphur were dissolved, and the residue looked much like the unaltered silicide. Dilute boiling nitric acid having no effect on it, it was at once treated with hydrofluoric acid. This left a small residue which contained some insoluble sulphur, some chromium, probably as sulphide, and a trace of silicon, probably due to iron silicide, $FeSi_2$. In this case also no silicon was liberated by the sulphur.

Action of Sulphur on Iron Silicide.

Iron silicide, containing 39.51 per cent. of combined and no free silicon, was boiled with sulphur in an open glass tube. The product does not have the odor of hydrogen sulphide, and the silicide remains quite unaltered.

It is shown again by these experiments that copper has much less affinity for silicon than other metals, such as iron, manganese, or chromium, and that it approaches in its conduct to silver, which only slightly combines with silicon. They also show that the affinity of copper for silicon is weak at a high temperature when the silicide dissociates, at a low temperature when acids easily attack it, and at a medium temperature when sulphur decomposes it completely, while other silicides remain practically unaltered.

WILLSON ALUMINUM CO.,
HOLCOMB'S ROCK, VA.

ACETYLENE DIIODIDE.

BY G. DE CHALMOT.

In the *Berichte*, Vol. 30, page 1200, there is an article by Mr. H. Biltz, on acetylene diiodide C_2I_2, and ethylene tetraiodide C_2I_4. Some years ago when engaged in an entirely different line of work, I ran across acetylene diiodide, and prepared it in very much the same manner as Mr. Biltz did. I do not wish to claim any priority, for I never gave the matter much attention.

I was preparing the ethylene tetraiodide (diiodoform) by the method of Maquenne, taking calcium carbide instead of barium carbide.[1] The alcoholic washings of the crude tetraiodide were diluted with water, and the diiodide of acetylene was precipitated, together with some oily matter.

[1] Bull. Soc. chim., [3], **7**, 777, 1892.

The diiodide crystallizes from alcohol or ether in long, transparent needles. I found the melting-point at 82° C. (Biltz finds 78° C.). I further found in my notes the following:

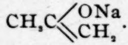
When I added iodine to a solution of acetylene in caustic potash solution, I did not obtain a trace of ethylene tetraiodide, C_2I_4, but I obtained a white precipitate. This was filtered off, and recrystallized from benzene. It forms white needles of a very pungent odor, which strangely affect the mucous membranes, especially of the eyes. An analogous compound can be made with bromine. It is an oil of very disagreeable odor. It takes fire spontaneously in contact with the air. Whether this is due to an admixture of bromacetylene, C_2HBr, or the compound itself has this property, I have not investigated.

WILLSON ALUMINUM CO.,
HOLCOMB'S ROCK, VA.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF SODIUM UPON METHYLPROPYLKETONE AND ACETOPHENONE.

BY PAUL C. FREER AND ARTHUR LACHMAN.

Some years ago one of us[1] showed that acetone is capable of forming a sodium derivative, whose behavior indicated the attachment of the metal to oxygen,  $CH_3C\begin{smallmatrix}\diagup ONa\\ \diagdown CH_2\end{smallmatrix}$. The chief reaction then studied showed the general analogy of the action of sodium acetone and sodium acetoacetic ether towards benzoyl chloride and towards chlorcarbonic ether, *viz.*, the simultaneous formation both of C- and O-derivatives in the first case, and of O-derivatives in the second. According to the present addition-hypothesis, this behavior finds its satisfactory explanation in the assumption of an oxy-structure of the sodium compounds. Recently[2] Freer found that acetaldehyde also forms a sodium derivative of similar structure, $CH_2{=}CHONa$. This sodium vinylate is extremely unstable, but its presence is proved by the simultaneous action of a mixture of acetaldehyde and benzoyl chloride upon finely divided sodium, resulting in the production of aldehydo-aldol benzoate,

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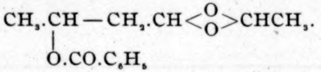
[1] This JOURNAL, **12**, 155; *Ibid*, **13**, 319; *Ibid*, **15**, 582; *Ibid*, **17**, 1.

[2] *Ibid*, **18**, 552.



$$\begin{array}{l} CH_3.CH - CH_2.CH\langle{}^{O}_{O}\rangle CHCH_3. \\ \quad\;\; | \\ \quad\;\; O.CO.C_6H_5 \end{array}$$

The existence of the above-mentioned sodium salts shows that it is by no means necessary for a methylene group to be adjacent to *two* carbonyls, in order that its hydrogen may be capable of replacement by metals. The object of the present investigation was to determine whether the property of forming sodium substitution-products is a general reaction of carbonyl compounds, or whether it is limited to the lower members of the acetone series. For this purpose, the behavior of methylpropylketone and acetophenone toward sodium was examined. The method employed was the one introduced during the study of sodium acetaldehyde, *viz.*, the combined action of the ketone and benzoyl chloride upon sodium suspended in ether.

Action of Sodium upon Methylpropylketone.

If sodium be allowed to act upon a dilute solution of methylpropylketone in ether, hydrogen is rapidly evolved, and a white, flocculent sodium compound is precipitated. This substance is fairly stable in dry air ; water decomposes it immediately. Analysis shows that it has the composition represented by the formula $C_5H_9O.Na$.

1.2131 grams gave 0.8272 gram sodium sulphate.

Found, 22.1 per cent. Calculated, 21.3 per cent.

Remembering the complex nature of sodium acetone, however, it is not likely that this analogous sodium compound is a definite individual.

The action of a mixture of the ketone and benzoyl chloride upon sodium proceeds with considerable energy, so that the presence of large quantities of ether, as well as frequent cooling in water, are necessary. The reaction is usually complete within a few hours. It is best to work with about five grams of sodium wire at a time, suspended in 250 cc. of absolute ether; a mixture of 20 grams ketone and 30 grams benzoyl chloride, diluted somewhat with ether, is dropped in slowly. The product of several such reactions may be readily worked up at once. For this purpose, water is added to dissolve the yellowish solid formed, and the ether solution shaken out with dilute alkali until on acidifying no turbidity is produced in the extract. The united extracts are then treated as under *A*, and the ether residue as in *B*.

A. The Alkaline Extract.

When the alkaline extracts are acidified, a large quantity of benzoic acid separates, together with a trace of an undetermined fatty acid, and a solid polyketone. The mixture is treated with cold alcohol, which leaves the solid ketone almost completely undissolved; the alcoholic extract contains only traces of compounds other than benzoic acid.

The Solid Polyketone from Methylpropylketone.—The yield of this substance is small—13 grams from 180 grams methylpropylketone. It is almost insoluble in cold alcohol or ether, but dissolves readily in boiling alcohol. It is best purified by repeated solution in the last-named solvent, from which, however, it invariably separates in an amorphous form on cooling. A variety of solvents were tried in the attempt to obtain a crystallized body, but without a successful result, the substance always separating in white flakes, which show no regular forms, even when greatly magnified. The ketone melts in the neighborhood of 115°, with slight variations, which will be discussed below. It is very difficult to make a combustion of the substance; the highest figures obtained agree well with each other, and with the composition of *dibenzoylmethylpropylketone*.

I. 0.1789 gram gave 0.1056 gram water and 0.5057 gram carbon dioxide.

II. 0.1757 gram gave 0.1045 gram water and 0.4954 gram carbon dioxide.

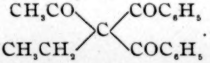
III. 0.1298 gram gave 0.0780 gram water and 0.3677 gram carbon dioxide.

	Calculated for		Found.		
	Monobenzoyl.	Dibenzoyl.	I.	II.	III.
C	75.8	77.5	77.0	76.9	77.3
H	7.3	6.1	6.7	6.6	6.7

Like all similar ketones, it colors ferric chloride intensely red. It is soluble in alkalies and carbonates, and is slowly precipitated from such solutions by carbon dioxide. Being similar in constitution to Claisen's dibenzoylacetylmethane,[1] it was expected that the new substance would likewise exist in two modifications; as a matter of fact, by varying the dilution of the alcohol used, as well as the rate at which the solution was allowed to cool, the melting-point would fluctuate between 101° and 115° and the ferric chloride reaction become occasionally very faint. But here too it was impossible to obtain crystalline products, so that nothing definite can be stated concerning the existence of the two isomers.

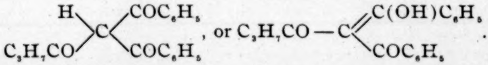
The constitution of the substance is determined by the fact that it is a dibenzoyl compound, and still possesses acid properties, of the two probable formulas, only the second corresponds to this condition:

I.



$$\begin{matrix}CH_3CO\\CH_3CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}COC_6H_5\\COC_6H_5\end{matrix}.$$

II.



$$\begin{matrix}H\\C_3H_7CO\end{matrix}\!>\!C\!<\!\begin{matrix}COC_6H_5\\COC_6H_5\end{matrix}, \text{ or } C_3H_7CO-C\!\begin{matrix}\diagup\!\!\diagup C(OH)C_6H_5\\ \diagdown COC_6H_5\end{matrix}.$$

Saponification with alkalies proceeds only very slowly; thus, 1.031 grams were warmed on the water-bath for two full days with excess of normal caustic soda solution, of which 6.7 cc. were neutralized, while 10.5 cc. are required for complete hydrolysis. This same sample gave 0.52 gram benzoic acid instead of 0.83 gram. The small quantity of butyryldibenzoylmethane at our disposal prevented any adequate investigation thereof. With phenylhydrazine it gives several products; one of them forms long needles, melts at 110°, and contains 8.8 per cent. nitrogen.

B. The Ethereal Residue.

This contained the main products of the reaction. It was dried over calcium chloride, and distilled at 10 mm. pressure. The distillation was conducted in small portions, and continued until the distillate began to solidify, *i. e.*, consisted of benzoic acid. There always remained a large quantity of non-volatile tar (130 grams from 180 grams ketone), which decomposed when strongly heated, yielding chiefly benzoic acid. The distillate was repeatedly extracted with sodium carbonate solution, dried, and carefully refractioned five times at 10 mm., when fractions were obtained as indicated below :

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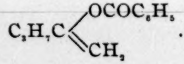
[1] Ann. Chem. (Liebig), **291**, 73.

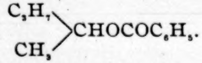
		Grams.
I.	Below 40°	3
II.	40°–75°	1
III.	75°–90°	8
IV.	90°–111°	6
V.	112°–117°	11
VI.	Above 117°	5

Fraction I. consisted of methylpropylketone ; *all* the others, without exception, contain chlorine. III. contained 11.4 per cent.; V. 3.2 per cent.; of an earlier preparation, the fraction corresponding to III. contained 8.5 per cent. ; that corresponding to V. contained 2.8 per cent. This chlorine is retained with the utmost tenacity ; it is not removed by repeated extraction with alkali, nor by distilling over sodium, nor finally by boiling for several days with a solution of caustic potash in methyl alcohol. The halogen is therefore present as a chlorine substitution-product. Combustions showed the various fractions to consist of mixtures.

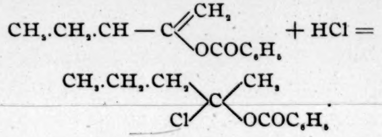
Fraction III.—Upon saponification with a solution of caustic potash in methyl alcohol, 2 grams gave 0.9 gram benzoic acid, 1 gram methylpropylketone, a trace of unchanged halogenated oil, and an undetermined quantity of hydrochloric acid. The fraction therefore contains the isoketone benzoate,



$C_3H_7C\begin{cases} OCOC_6H_5 \\ CH_2 \end{cases}$. This is further shown by the fact that 1 gram absorbed 0.26 gram bromine without evolution of hydrobromic acid. (Calculated for pure benzoate, 0.80 gram.) No methylpropylcarbinol was observed in this fraction, the portion of the oil which does not take up bromine also yielding methylpropylketone on saponifying. This saturated compound probably consists of a hydrochloric acid addition-product of the isoketone benzoate, and will be discussed below.

Fraction V.—The products of saponification here were as follows: 6.2 grams gave 3.2 grams benzoic acid, and undetermined quantities of hydrochloric acid, a trace of unchanged oil, and a liquid which did not react with sodium bisulphite, boiling at 114°. This liquid is therefore methylpropylcarbinol, and the fraction consists chiefly of its benzoate,  $\begin{matrix} C_3H_7 \\ CH_3 \end{matrix}\!\!>\!CHOCOC_6H_5$. This again is borne out by the bromine-absorption, for 1 gram took up less than 0.3 gram thereof.

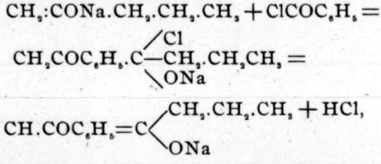
These fractions would thus seem to be mixtures inseparable by distillation; their most remarkable feature being the large amount of chlorine they contain. This chlorine could only have come from the benzoyl chloride; and as benzoyl chloride is not an active chlorinating agent, especially in the presence of an excess of sodium, the halogenated compounds can only have been formed from *intermediate addition-products*. This occurrence of halogen compounds is characteristic of all such reactions; for we have come upon the same phenomenon with acetophenone, and a preliminary trial showed quite a quantity of halogen in the product of the action of benzoyl chloride on sodium acetoacetic ether. A clue exists as to the nature of these halogenated bodies. The saponification of Fraction III. gave nothing but benzoic acid, methylpropylketone, and hydrochloric acid; the bromine-absorption showed the presence of only one-third of the *unsaturated* isoketone benzoate; the other two-thirds then consisted of the hydrochloric acid addition-product of this benzoate:



$$CH_3.CH_2.CH - C\begin{matrix} \diagup CH_2 \\ \diagdown OCOC_6H_5 \end{matrix} + HCl =$$

$$\begin{matrix} CH_3.CH_2.CH_2 \\ Cl \end{matrix}\!\!>\!C\!<\!\begin{matrix} CH_3 \\ OCOC_6H_5 \end{matrix}.$$

The origin of the hydrochloric acid is therefore to be sought in the breaking down of the addition-product of benzoyl chloride to sodium methylpropylketone :



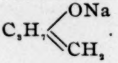
$$CH_2{:}CONa.CH_2.CH_2.CH_3 + ClCOC_6H_5 =$$

$$CH_2COC_6H_5.C\begin{matrix}/Cl\\ -\\ \backslash ONa\end{matrix}CH_2.CH_2CH_3 =$$

$$CH.COC_6H_5{=}C\begin{matrix}/CH_2.CH_2.CH_3\\ \backslash ONa\end{matrix} + HCl,$$

into *hydrochloric acid* and *sodium monobenzoyl methylpropylketone*, in accordance with Nef's hypothesis. The sodium monobenzoyl compound would then react with more benzoyl chloride to give the above described solid butyryldibenzoylmethane, again separating hydrochloric acid. The latter substance, in absolute ethereal solution, therefore, apparently more readily *adds* itself to the unsaturated isoketone benzoate than it liberates free methylpropylketone mono or dibenzoyl methylpropylketone from their sodium derivatives. That a portion of the acid is used in the latter way, is, however, proved by the fact that considerable quantities of methylpropylketones are recovered from the neutral oil. We were not able to find any monobenzoylketone, which shows that none of the latter compound was set free by the acid.

Summing up the action of benzoyl chloride upon sodium methylpropylketone, then it is in its general course similar to that with sodium acetone, and it is reasonable to ascribe a similar constitution to the sodium compounds. As the solid dibenzoylketone contains its benzoyl groups attached to the methyl, sodium methylpropylketone has the following structure:



$$C_3H_7C\begin{matrix}/ONa\\ \backslash\backslash CH_2\end{matrix}.$$

The Action of Sodium upon Acetophenone.

Some years ago, Beckmann and Paul[1] undertook the investigation of the action of sodium upon acetophenone. The compound they obtained, upon treatment with water, regen-

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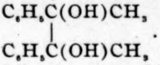
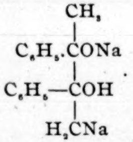
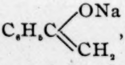
[1] Ann. Chem. (Liebig), 266, 18.

erated acetophenone, as well as acetophenone-pinacone I,

$$\begin{array}{l} C_6H_5C(OH)CH_3 \\ \quad | \\ C_6H_5C(OH)CH_3 \end{array}$$
. Upon this as a basis, they ascribed the following formula to the substance:


$$\begin{array}{r} CH_3 \\ | \\ C_6H_5.CONa \\ | \\ C_6H_5—COH \\ | \\ H_2CNa \end{array}$$
.

Such a formula, as has been pointed out in a previous paper,[1] is extremely improbable; the more so when the observation which led to it, *viz.*, the production of the pinacone with water, is readily explained by the pre-existence of sodium acetophenone-pinacone in the so-called sodium salt. As it had been previously shown by one of us[2] that sodium acetone also contains sodium pinacone, as well as sodium derivatives of higher condensation-products of acetone, it undoubtedly is true that sodium acetophenone is not a pure body. Recently Beckmann and Schliebs[3] determined the molecular weight of sodium acetophenone; they obtained no satisfactory measurements, but emphasize the fact that a *lower* molecular weight than that deduced from chemical observation was not obtained.

Our investigation of the action of sodium upon acetophenone, carried out in the manner described above, shows that acetophenone behaves just as do acetone and methylpropylketone, and that to a large extent, at any rate, sodium acetophenone is monomolecular,  $C_6H_5C\begin{cases} ONa \\ CH_2 \end{cases}$, so far as can be judged from its reaction with benzoyl chloride.

105 grams of acetophenone and 120 grams benzoyl chloride, diluted with 250 cc. ether, were allowed to drop slowly upon 20 grams of sodium wire suspended in 1500 cc. ether; the ether was kept gently boiling all the while. When the odor

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[1] This JOURNAL, **15**, 582.

[2] This JOURNAL, **15**, 587.

[3] Ann. Chem. (Liebig), **289**, 81, (1895).

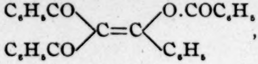
of benzoyl chloride had disappeared, the mixture was treated with water and extracted with alkali until all soluble products had been removed.

A. Alkali Soluble Products.

The extract was acidified, and the precipitated solid extracted several times with boiling alcohol. 26 grams of crude *tribenzoylmethane* remained, which upon recrystallization from boiling acetone, melted at 223°, and showed all the characteristic reactions described by Claisen.[1] The alcoholic solution was evaporated to dryness, and then treated with dilute soda solution, whereby all except 0.5 gram was dissolved; the remainder colored ferric chloride intensely, and smelled strongly of *dibenzoylmethane*, but the amount was too small for the purification of a compound so soluble and difficult to purify. No other products could be found in the alkaline extract, except large quantities of benzoic acid.

B. Ether Solution.

This was first distilled at 14 mm. in order to remove all volatile constituents. There passed over 21 grams oil, which contained 3.8 per cent. chlorine; upon careful refractioning at ordinary pressure, it gave about 17 grams acetophenone, and a higher-boiling residue, which contained most of the halogen. The acetophenone solidified completely with phenylhydrazine, and therefore contained no phenylmethylcarbinol. The residue, after the vacuum distillation, consisted of a thick tarry mass. It was carefully saponified by allowing it to stand for a day with a solution of caustic potash in methyl alcohol, and finally warming it for a few minutes upon the water-bath. Upon acidification, the alkaline solution yielded benzoic acid and *tribenzoylmethane* (M. P. 222°, characteristic needles from acetone). The tar therefore contained among other products the benzoate of tribenzoylmethane,



$$\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix} \Big> C{=}C \Big< \begin{matrix} O.COC_6H_5 \\ C_6H_5 \end{matrix}$$

, described by Claisen.

Another portion of the tar was saponified by heating it to 160° with dilute sulphuric acid for twenty hours. The products contained were ***benzoic acid***, ***acetophenone-pinacone*** (colorless prisms, M. P., 120°.5, insoluble in soda), a ***ketone*** boiling at 180°–182° at 14 mm., and a large amount of tarry residue. The ketone contains halogen, colors ferric chloride deeply, is insoluble in alkalies, and reacts slowly with phenylhydrazine; it has not yet been investigated further. Particular pains were taken to find acetophenone among the products of saponification by sulphuric acid, but without success; after removing the benzoic acid, and distilling at 14 mm., the thermometer rose at once to 120°, the distillate solidifying immediately, and consisted of the pure pinacone.

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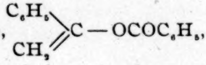
[1] Ann. Chem. (Liebig), 291, 90.

Acetophenone thus shows the same behavior towards sodium in the presence of benzoyl chloride, as is manifested by acetone and methylpropylketone, with the exception that *no* isoketone benzoate,  $\begin{matrix} C_6H_5 \\ CH_2 \end{matrix} \!\!> C - OCOC_6H_5$, as would be shown by presence of acetophenone in the products of saponification, could be found.

It would seem that the more negative character of the ketone tends to suppress the formation of the O-derivatives with benzoyl chloride; thus acetone gives a considerable yield, methylpropylketone much less, acetophenone and acetoacetic ether apparently none at all. To all intents, it is a difference in degree rather than in kind of reaction.

The large quantities of tarry condensation-products seem to be the chief result of the reactions above described. For this reason the experimental investigation of other ketones scarcely promises to repay the labor necessary. However, we add a few experiments with mesityl oxide, which go to show that it is extremely probable that the property of forming sodium substitution-products is a general one with carbonyl compounds.

The Action of Sodium on Mesityl Oxide.

Pure colorless mesityl oxide, of constant boiling-point,[1] reacts so energetically with sodium that the products may even take fire with explosive violence. If the ketone is somewhat diluted with ether the action goes on more quietly. The resulting sodium compound is at first white or slightly yellow, but it soon turns to a dark red, exactly as is the case with sodium acetone. In order, if possible, to isolate the sodium compound, 1.3 grams of sodium wire were covered with absolute ether, placed in a flask with double-bored stopper, such as is described in the preparation of sodium acetone,[1] the flask was filled with pure hydrogen, covered with snow, and then an excess of mesityl oxide was gradually added. The reaction proceeded quietly and slowly, but in spite of all precautions we were not able to filter, wash and dry the sodium compound before considerable decomposition had set in, and as a consequence, no satisfactory analyses could be obtained. Warming the solution promptly turned the sodium compound deep red. A portion of the sodium compound is soluble in ether just as in the case with sodium acetone, but here also all attempts to isolate the compound failed because of the ready decomposition of the body. The sodium compound readily reacts with benzoyl chloride, the ether boils and the liquid changes to a dark-green color, which finally gives way to amber; when the latter change takes place, the action is complete. The contents of a number of flasks were united, and the ethereal solution washed with water; when the aqueous solution was acidified large quantities of benzoic acid were precipitated, as is usual with these reactions. The ethereal solution was extracted with 10 per cent. caustic potash, and the latter was supersaturated with carbon dioxide. Only a small quantity of an oil separated, and this could not be purified. On acidifying the bicarbonate solution with hydrochloric acid benzoic acid separated.

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[1] A very good yield of pure mesityl oxide is obtained by saturating acetone in a freezing-mixture with gaseous hydrogen chloride, allowing to stand for about half an hour and then pouring the liquid into ice-water. The mesityl oxide, which separates, is then washed with water and dilute alkalies, and fractioned after drying. By this

The ethereal extract was dried over calcium chloride, the ether evaporated, and the product, which contained considerable quantities of halogen, was then fractioned under reduced

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method the formation of phoron is almost completely prevented. The yield is much better than it is by Claisen's method. (Ann. Chem. (Liebig), **180**, 4.) The difference lies in not allowing the acetone to stand for any length of time after being saturated with hydrogen chloride. Acetone can be recovered from the wash-water.

[1] This JOURNAL, **15**, 588.

pressure. The first fraction contained unchanged mesityl oxide; the higher fractions were evidently condensation-products of that body; finally, above 170°, at 50 mm. pressure, large quantities of benzoic acid separated, and the distillation was interrupted. No definite substance could be separated from the lower boiling fractions. They behaved like the condensation-products of acetone. On saponification the higher portions yield benzoic acid. As the continuation with mesityl oxide did not seem to promise results of sufficient interest, further work was not undertaken. Enough has, however, been done to show that mesityl oxide behaves toward sodium much as acetone does. The difficulties in the way in the study of mesityl oxide are much greater than in that of the other ketones, owing to the ease with which it forms higher condensation-products. No better results were obtained when acetyl chloride was substituted for benzoyl.

Diethylketone, in ethereal solution, readily reacts with sodium, and a gas, which analysis proved to be hydrogen, passes off. The resulting sodium compound is white in color and its properties resemble those of the other sodium compounds prepared. Sodium diethylketone seems to be more stable than sodium acetone or sodium methylpropylketone. No further work has been done with this body.

The most curious phase of these reactions, which so far as we are aware, has never been pointed out, is the fact that large quantities of oils containing halogen are formed by the action of benzoyl chloride on the sodium derivatives of ketones, and one of us observed the same phenomenon while working with chlorcarbonic ester and sodium acetone. This fact adds to the complexity of a synthetic change which has already been the subject of so much discussion. Another feature to which attention should especially be called is the large quantity of benzoic acid which is always recovered as a result of the reactions between benzoyl chloride and sodium ketones. Evidently the halogenated bodies can only be produced by a separation of hydrogen chloride from an addition-product and its subsequent addition to the unsaturated body so produced, as was pointed out in the previous portion of this work and, very likely, the benzoic acid also takes its origin in a separation from a similar addition-product. The addition theory of Michael[1] seems now to be quite widely accepted as an explanation of the first phase of these reactions (in the cases where C-acyl compounds are produced) the difference of opinion touching the point whether the subsequent separation is one of halhydric acid or of sodium halide. The work with sodium acetone, methylpropylketone and acetophenone shows that a portion of the reaction must certainly take place with the separation of halhydric acid, because of the halogenated oils produced, but at the same time another phase of the reaction must yield benzoic acid, while it is not at all improbable that in a third direction sodium halide is also separated. With sodium acetoacetic ether the reaction does not seem to give free benzoic acid as in the acetone series, but the halogenated bodies are produced. In this case the reaction is therefore less complicated. Claisen's[2] explanation of the formation of sodium dibenzoylmethane is another phase of these reactions which undoubtedly takes place in many cases, so that we have come to the conclusion that no simple explanation will cover all the facts in any one of these reactions, and also that no general law can be deduced which will cover all cases, but that the main direction of any one reaction can only be discovered by a careful study of the particular case in question.

ANN ARBOR, JULY, 1897.

SOLUBILITY OF LEAD IN AMMONIA.

BY H. ENDEMANN.

Some years ago my attention was forcibly drawn to the possibility, that the ammonia of commerce may contain lead. Quantitative determinations of traces of lead in an organic acid were made in my laboratory, and in a western laboratory, and gave results which were low here and high in the west. My method consisted in incinerating the acid and determining the lead in the ash. The western method consisted in neutralizing the acid by ammonia, then adding ammonium sulphide, and separating and determining the lead in the precipitate thus obtained. The western method gave in my hands practically the same result as my incineration method. Meanwhile, the high results continued in the west.

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[1] J. prakt. Chem., **37**, 473.

[2] Ann. Chem. (Liebig), **291**, 54.

Inasmuch as the only reagent used in large quantity in the saturation method was ammonia, I concluded that, notwithstanding the fact that no mention had been made and published, embodying such observation, ammonia must be capable of dissolving lead in the presence of air. An experiment proved this to be correct.

The lead found in the organic acid by this method was, therefore, in part derived from the ammonia used in the analysis. Hence the difference between the results was explained.

Since, I have repeatedly had occasion to revert to this fact in one form or another, and have been unable to find any satisfactory explanation in the literature bearing upon this subject, I have finally concluded to publish my results.

In the literature but few statements can be found bearing upon the solubility of lead oxide on ammonia. The oldest statement is by Karsten, who says that lead dissolves in ammonia, forming a dark-yellow solution.

The last mention is found in the *Comptes rendus* for 1846, wherein Calvert doubts the existence of an amide of lead. Later publications are all to the effect that lead oxide is insoluble in ammonia. In all books on analytical chemistry, the statement occurs that lead salts are precipitated by ammonia "insoluble in excess."

I, myself, could not get the yellow solution of which Karsten speaks, by using litharge and the strongest ammonia in the cold, and allowing the action to proceed for weeks. I obtained no trace of lead in solution. The ammonia contained, however, some zinc, which must have been an impurity of the litharge.

If lead is immersed in the strongest ammonia (29 per cent.), there is within the first day or so, apparently no change. The ammonia remains perfectly clear and the lead shows no changes. If, however, the ammonia is tested for lead it will be found to contain quite a quantity. On allowing to stand for some time longer, the ammonia solution still remains clear, but the lead will be found coated with a colored substance. This coating is at first orange, later decidedly rust-colored as long as it remains in contact with the lead. The dark color of the coating fades quickly after the precipitate has been mechanically loosened from the metal.

After three days' action the ammonia solution contains 0.0139 per cent. lead, or 13.9 parts in 100,000 parts. The coating removed from the sheet-lead by a quick action of dilute acid, contained 0.0569 gram of lead. By allowing the action to proceed for weeks, a white precipitate is formed upon the bottom and sides of the vessel, which appears to be mainly lead hydroxide, mixed with oxides of other metals. Of ammonia, it contains only 0.15 per cent. after drying. During this long standing the ammonia had gradually become less concentrated.

If in the place of 29 per cent. ammonia, 2.9 per cent. ammonia water is taken, the oxidation of the lead is quite as lively, but the appearances differ. In twenty-four hours a white precipitate is visible upon the glass, the surface of the liquid, and upon the lead, which greatly increases during the next forty-eight hours.

The lead is partly in solution, but present mostly as precipitate. The lead in both forms together in 100 cc. of such ammonia, amounted to 0.0922 gram, or 92.2 parts for 100,000 parts of the liquid. The precipitate is also in this case apparently the hydrated oxide of lead.

The rapidity of oxidation is evidently not due to the greater or less amount of ammonia present in the experiment. In the experiment with the weaker ammonia the oxidation has been even more rapid. Whether this is due to a slightly greater surface of the lead sheets used, or to the fact that the stronger ammonia excludes the air from the flasks, and thus impedes oxidation, I have not attempted to decide. All observations tend to point to a suboxide of lead as the body soluble in ammonia; for instance, the fact that the clear solution of lead in concentrated ammonia becomes turbid on exposure to air. These observations are of considerable practical utility. In the first place, in the manufacture of ammonia water, lead linings and connections for absorption tanks should be omitted. Some such use evidently laid the foundation for my own observations. But its main importance is derived from the possible contamination of waters which have been softened by the addition of lime-water. It is a well-known fact that waters which contain bicarbonate of lime act hardly, or not at all, upon lead. To this observation may be added my own, that bicarbonate of ammonia likewise does not act upon lead. If water containing bicarbonate of lime and ammonia is softened with quicklime, the danger of destroying lead pipes becomes at once evident, if we consider that thereby the formation of some free ammonia may be caused. I should mention, however, that caustic lime is about as dangerous as ammonia. Lead dissolves quite easily in lime-water in the presence of air. Therefore, even in the absence of ammonia salts, lead may be destroyed, if proper care is not taken that the lime shall at no time be in excess.

Rain waters, which do not contain any quantity of fixed bases, but mainly ammonia salts, may at any time by loss of acid as, for instance, reduction of nitric and nitrous acid by reason of putrefaction, contain free ammonia, and then become destructive to lead while they themselves become contaminated.

In the literature we quite frequently find examples in which water apparently did not act upon lead according to the accepted notions, and in such cases it might be worth while to consider the bearings of the above facts for a probable explanation of such anomalies.

23 WILLIAM ST., NEW YORK.

THE DECOMPOSITION OF SULPHONIC ETHERS BY WATER, ACIDS AND SALTS.[1]

BY J. H. KASTLE, PAUL MURRILL, AND JOS. C. FRAZER.

Some time ago Kastle and Murrill[2] made a study of the saponification of the sulphonic ethers by alcohols. The results obtained at that time encouraged us to try the effect of water upon the sulphonic ethers, in order that a comparison might be made between it and the alcohols in the rate of change. At the outset, however, we were confronted with the difficulty that the sulphonic ethers are insoluble, or nearly so, in water. The essential preliminary, therefore, to work in this direction, was to find a solvent which would dissolve both the ether and water, and would in itself be without action on the ether. Pure acetone was finally selected as the solvent most nearly filling these requirements. This substance was found to dissolve the sulphonic ethers very readily, and to such a solution water could be added in considerable quantities without causing a precipitation of the dissolved ether. It was found, further, that the sulphonic ether could be heated with say 50 molecules of acetone, without undergoing any appreciable alteration.

The ethyl ether of *p*-brombenzenesulphonic acid was chosen for the work, as being probably the best and most available representative of this class of compounds for these experiments. This ether is readily obtained pure in considerable quantity, and is rapidly decomposed under the conditions of our experiments. The manner of conducting these experiments was as follows: The thousandth part of the molecular weight of the brom-ether in grams (0.265 gram) was dissolved in 50 gram-molecules of acetone, *viz.*, 37 cc.; and to this solution there was then added 50 times the theoretical quantity of water or ethyl alcohol, *viz.*, 0.9 cc. of water, and 2.9 cc. ethyl alcohol. These solutions were put into glass bulbs of convenient size, which were then sealed and placed in a thermostat, and kept at the desired temperature, 98° C., for different intervals of time, at the end of which the bulbs were opened and their contents titrated with $\frac{N}{10}$ caustic potash. The following results were obtained :

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[1] Abstract of a paper read before the American Association for the Advancement of Science, at the Buffalo Meeting, 1896.

[2] This JOURNAL, 17, 290.

Table No. 1.

Water.			Ethyl alcohol.		
Time.	Per cent. decomposed.	K.	Time.	Per cent. decomposed.	K.
20 min.	41.58	0.02723	20 min.	14.9	0.00806
30 "	55.44	0.02736	30 "	20.83	0.00779
40 "	66.33	0.02771	40 "	25.62	0.00739
50 "	74.25	0.02772	50 "	31.49	0.00756
60 "	81.1	0.02776	60 "	35.51	0.00731
90 "	92.1	0.02820	70 "	40.53	0.00742
			80 "	44.72	0.00740
	Mean =	0.02766	90 "	49.74	0.00789
			100 "	54.6	0.00789
			120 "	57.95	0.00721
				Mean =	0.007593

On comparing the values of K for water and alcohol, it will be observed that the velocity of the reaction for water is about 3.5 times as great as that for ethyl alcohol. Such a result is in keeping with what is generally known as to the activity of these two compounds.

Action of Acids and Salts on Ethyl p-brombenzenesulphonate.

In view of the very interesting and important results obtained by Ostwald in the study of the influence of acids on the hydrolysis of methyl acetate, it was deemed expedient to make similar studies with the sulphonic ethers. Having this for their object, a number of experiments were tried as follows : 0.9 cc. of water and of normal and $\frac{N}{10}$ solutions of several acids and salts, were heated for thirty minutes in boiling water with 0.265 gram ether and 3 cc. acetone. At the end of this time the amount of decomposition was measured by titrating with $\frac{N}{10}$ caustic potash ; the results of these experiments are given in Table II.

Table No. II.

Normal solutions.	Per cent.
Hydrochloric acid	26
Hydrobromic acid	21
Formic acid	63
Acetic acid	61
Butyric acid	61
$\frac{1}{2}$-N sulphuric acid	70
Nitrotoluene sulphonic acid	59
$\frac{1}{2}$-N oxalic acid	67
Calcium nitrate	55
Calcium chloride	40.5
Magnesium chloride	44.5
Sugar	67
Water	70

$\frac{1}{10}$-N Solutions.	Per cent.
Hydrochloric acid	63.31
Hydrobromic acid	63.3
Formic acid	71.5
Acetic acid	70.
Butyric acid	72.66
$\frac{1}{20}$-N sulphuric acid	70.
Potassium chloride	60.7
Sodium chloride	59.71
Sodium acetate	66.01
Potassium nitrate	66.43
Sugar	70.52
Glucose	67.9

By comparing the amount of decomposition for each substance in the above table with that of water alone, it will be observed that nearly all acids and all salts greatly retard the decomposition of the sulphonic ether—a result which is entirely at variance with those reached in the study of the hydrolysis of methyl acetate ; and one for which, for a time, no explanation could be given. It was soon found, however, that the retardation produced by acids and salts was only apparent—not real, and further, that caustic potash alone does not afford the means of measuring the decomposition of a sulphonic ether in aqueous solutions of acids and salts. An experiment with potassium iodide[1] and the brom-ether in alcoholic solution gave the clue to the correct interpretation of the above results. 0.265 gram of ethyl *p*-brombenzenesulphonate was heated for thirty minutes with 1 cc. normal solution of potassium iodide and 3 cc. alcohol. After titrating with alkali, the solution was poured into water when the characteristic odor of ethyl iodide was observed. The solution was then boiled, in order to get rid of the ethyl iodide, and titrated with $\frac{N}{10}$ silver nitrate. It took 1.9 cc. to precipitate the iodide remaining in the potassium iodide. Had all of the iodide remained unchanged, 10 cc. of $\frac{N}{10}$ silver nitrate would have been required to precipitate the iodine. Hence 81 per cent. of the potassium iodide had reacted with the sulphonic ether to form ethyl iodide and potassium *p*-brombenzenesulphonate, and only 19 per cent. of the potassium iodide remained unchanged. Similarly, it was found in the case of hydrochloric acid that this substance reacted with the sulphonic ether to form ethyl chloride and the sulphonic acid. Hence the change which takes place when an acid or a salt acts on a sulphonic ether cannot be measured by a standard solution of alkali alone. Such being the case, the results in Table II. are altogether misleading. It is really necessary to make two measurements, in order to determine what has taken place in such a solution. One, of the increase in acidity, by means of caustic potash, and another, by means of silver nitrate, of the quantity of halogen[2] which remains as halide. For at the same time that reaction is taking place between the acid or salt and the ether, decomposition also occurs between the ether and water, so that in such a solution two changes are taking place simultaneously, one according to equation (1), another according to equation (2).

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[1] Since this experiment was tried, Mr. A. S. Loevanhart has succeeded in obtaining ethyl iodide in quantity by the action of potassium iodide upon large amounts of ethyl *p*-brombenzenesulphonate, in solution in alcohol, and also in acetone, at the temperature of the water-bath, thus proving that the action of potassium iodide on a sulphonic ether is altogether analogous to its action on a salt of ethylsulphuric acid.

[2] Of course, other acids and salts, besides the halides, may react with the sulphonic ether. In fact, it is known that this is the case. In many instances, however, it would be almost impossible to measure rapidly the amount of acid or salt remaining unacted on; and hence the halide acids and salts have alone been employed in the investigation thus far, for the reason that the halogen remaining unchanged can be rapidly estimated by means of silver nitrate. We hope, in the near future, however, to try other acids and salts.

$$(1)\ RSO_2C_2H_5 + M.Hl^1 = R.SO_2OM. + C_2H_5Hl.$$
$$(2)\ RSO_2OC_2H_5 + HOH = R.SO_2OH + C_2H_5OH.$$

Such being the case, a number of experiments have been tried, in which both measurements have been made. In these last experiments a standard solution of the sulphonic ether in acetone was made of such concentration, that 4 cc. of it contained the thousandth part of weight in grams of the ether, *viz.*, 0.265 gram. These portions of 4 cc. each were placed in tubes of convenient size, and into each there was then introduced 1 cc. of water or a normal solution of the acid or salt. The tubes were then sealed, and allowed to remain at ordinary temperatures or heated, for the desired interval of time, at the end of which they were opened and their contents titrated, first with $\frac{N}{10}$ caustic potash, and then with $\frac{N}{10}$ silver nitrate. The results of these experiments with acids and salts are given in Tables III and IV:

Table III.

Showing the rate of decomposition of a sulphonic ether by water, acids, and salts.

Series No. 1, ordinary temperature, time, 10 days. Experiment.	$\frac{N}{10}$ caustic potash taken.		$\frac{N}{10}$ silver nitrate taken.		Percentage of ether decomposed by water.	Percentage of ether decomposed by acid or salt.	Total decomposition.
(1) With 1 cc. water	4.4	cc.	..	cc.	44.	..	44.
(2) " 1 " N-HCl	11.6	"	2.8	"	16.	72.	88.
(3) " 1 " N-HBr	11.3	"	1.8	"	13.	82.	95.
(4) " 1 " N-KI	0.8	"	0.6	"	8.	94.	102.
(5) " 1 " $\frac{N}{2}$-MgCl$_2$	2.4	"	4.4	"	24.	44.	68.
(6) " 1 " $\frac{N}{2}$-CaCl$_2$	2.5	"	4.4	"	25.	44.	69.
Series No. 2, ordinary temperature, time, 31 days.							
(1) With 1 cc. water	9.2	cc.	..	cc.	92.	..	92.
(2) " 1 " N-HCl	12.6	"	2.4	"	26.	76.	102.
(3) " 1 " N-KI	1.7	"	2.2	"	17.	78.	95.
(4) " 1 " $\frac{N}{2}$MgCl$_2$	3.4	"	3.25	"	34.	67.5	101.5
(5) " 1 " $\frac{N}{2}$CaCl$_2$	3.4	"	3.3	"	34.	67.	101.

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[1] Hl is here suggested as the proper symbol for halogen.

Series No. 3, ordinary temperature, time, 32 days. Experiment.	$\frac{N}{10}$ caustic potash taken.	$\frac{N}{10}$ silver nitrate taken.	Percentage of ether decomposed by water.	Percentage of ether decomposed by acid or salt.	Total decomposition.
(1) With 1 cc. water	9.35 cc.	.. cc.	93.5	..	93.5
(2) " 1 " N-HCl	12.5 "	2.4 "	25.	76.	101.
(3) " 1 " N-HBr	12. "	1.8 "	20.	82.	102.
(4) " 1 " N-KI	1.95 "	2.6 "	19.5	74.	93.5
(5) " 1 " $\frac{N}{2}$-$MgCl_2$	3.3 "	3.2 "	33.	68.	101.
(6) " 1 " $\frac{N}{2}$-$CaCl_2$	3.4 "	3.2 "	34.	68.	102.
Series No. 4, temperature = 100° C., time, 40 minutes.					
(1) With 1 cc. water	8.3 cc.	..	83.	..	83.
(2) " 1 " N-HBr	11.9 "	2. cc.	19.	80.	99.
(3)[1] " 1 " $\frac{N}{2}$-$MgCl_2$	5.1 "	6.3 "	51.	37.	88.
(4)[1] " 1 " $\frac{N}{2}$-$CaCl_2$	5. "	7. "	50.	30.	80.

Table IV.

Showing the decomposition of the sulphonic ether by normal hydrochloric and hydriodic acids.

Temperature 98° C. Experiment.	Time.	$\frac{N}{10}$ caustic potash taken.	$\frac{N}{10}$ silver nitrate taken.	Percentage of ether decomposed by water.	Percentage of ether decomposed by acid.	Total decomposition.
(1) With 1 cc. N-HCl	5 min.	11. cc.	5.9 cc.	10.	41.	51.
(2) " 1 " "	10 "	11.35 "	3.9 "	13.5	61.	74.5
(3) " 1 " "	15 "	11.95 "	3.2 "	19.5	68.	87.5
(4) " 1 " "	20 "	11.8 "	2.9 "	18.	71.	89.
(5) " 1 " "	25 "	12. "	2.5 "	20.	75.	95.
(6) " 1 " "	30 "	12. "	2.4 "	20.	76.	96.
(1) With 1 cc. N-HI	30 min.	11.3 cc.	1.3 cc.	13.	87.	100.
(2) " 1 " "	45 "	11.2 "	1.4 "	12.	86.	98.
(3) " 1 " "	60 "	11.5 "	1.8 "	15.	82.	97.

These results are of interest first, as showing that acids and salts in solution in water and acetone decompose a sulphonic ether much more rapidly than water alone.[1] This difference in the velocity of the reaction for acids and water is in keeping with modern theoretical conceptions as to the nature of a salt or acid in solution. Being dissociated, these substances react more rapidly than water. Secondly, considerable interest attaches to these results and to this reaction, in consequence of the fact that but few chemical changes are known in which electrolytes and water react simultaneously and sufficiently slowly to enable one to follow the course of the reaction.

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[1] This is true in every substance except two. See Table III., Series No. 4, Experiments 3 and 4, and these exceptions may be due to experimental error.

As is usually the case, a rise of temperature causes a great increase in the velocity of the decomposition ; in the case of hydrochloric acid, for example, as great a change occurred in twenty minutes, at 98° C., as was brought about in ten days at ordinary temperature. Further, it would seem, in some cases at least, that the distribution of decomposition between the acid and water was independent of the temperature; for example, in the case of hydrochloric acid at ordinary temperature, 72 per cent. of the ether was decomposed by the acid and 16 per cent. by water, whereas at 98° C., 71 per cent. of the ether was decomposed by the acid and 18 by water. So in the same way, in the case of hydrobromic acid, at ordinary temperature, 82 per cent. of the ether was decomposed by the acid and 20 by water ; and at 100° C., in forty minutes, it was found that 80 per cent. of the ether had been decomposed by the acid and 19 per cent. by water. It will be observed further that acids and salts of analogous nature exert about the same influence upon the course of the reaction. Hydrochloric, hydrobromic, and hydriodic acids decompose the sulphonic ether to nearly the same extent ; this is notably the case also with magnesium and calcium chlorides.

We have already called attention to the many interesting differences existing between the carbonic and sulphonic acids.[1] There are none more interesting, however, than that presented in the action of acids and salts on the ethers of these two types of acids. On the ethers of the carbonic acids, acids act by contact, and, without apparently suffering any decomposition themselves, greatly accelerate the action of water on the ethers ; whereas, perfectly neutral salts seem to be without action upon them. On the sulphonic ethers, on the other hand, both acids and salts react in such a way as to effect a double decomposition between themselves and the ethers. In the former case the acid acts by contact; in the latter it is actually decomposed. As to the real cause of this difference in the conduct of these two types of ethers towards acids and salts, nothing of value can be said at present. In fact, no satisfactory explanation of the catalytic action of acids on the ethereal salts of the carbonic acids has ever been offered; and until we are better able to follow the part played by the acid, in its rôle as a hydrolyzing agent, speculation as to this difference in their conduct towards the carbonic and sulphonic ethers can be of little, if any, service.

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[1] Am. Chem. J., **17**, 290.

As stated in the above, one serious difficulty has stood in the way of the investigation of the decomposition of the sulphonic ethers by water and acids, and that is the insolubility of these ethers in water. Ethyl sulphonic acid, however, may be regarded as a sulphonic ether of the type represented by the formula $HO.SO_2OC_2H_5$. This compound and its salts are very soluble in water, and it is decomposed both by water and also by acids, so that it would seem to be a substance which would lend itself particularly well to the further investigations of this subject. This investigation is now in progress.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, July, 1896.

A STUDY OF ZINC HYDROXIDE IN PRECIPITATION.[1]

BY VERNON J. HALL.

Zinc hydroxide is a precipitate closely related in its nature by ferric hydroxide. Its chief difference lies in the fact that it is soluble in excess of alkali, while the latter is not. With the object in view of determining its action towards substances in solution, I have made a study of zinc hydroxide along the same line as that followed in the case of ferric hydroxide.[2]

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[1] For additional results obtained in this laboratory upon this subject, see article by Linebarger: J. Am. Chem. Soc., **17**, 354.

[2] This JOURNAL, **19**, 512.

Solutions.

In addition to the dilute solutions of potassium hydroxide and sulphuric acid mentioned in connection with the work upon ferric hydroxide, I used a solution of zinc chloride, made by dissolving 13 grams of zinc in hydrochloric acid, evaporating the excess of acid and making up to one liter with water (18½° C.). Owing to slight impurities in the zinc, I made gravimetric determinations of zinc, together with determinations of the chlorine present in this solution.

General Method.

Here, as in the work upon ferric hydroxide, the composition of the precipitate was obtained by subtracting the quantities of each constituent found in the "Filtrates" from the "Totals."

Series IV.

The first experiments were made to determine the action of zinc hydroxide upon the chlorine in a system constituted according to the following equation :

$$ZnCl_2 + 2KOH = Zn(OH)_2 + 2KCl.$$

I made up a system as follows : Into a 500 cc. flask I introduced 50 cc. of zinc chloride solution and added potassium hydroxide equivalent to two molecules, and enough more to neutralize the free acid of the solution of zinc chloride. The system thus constituted was then made up to 500 cc. with water (18½° C.). Of the mixture of solution and precipitate, well stirred, I drew off two or more portions of 50 cc. each, in which, after dissolving the precipitate with nitric acid, I made determinations of the total chlorine in the system. It will be observed that I made the determinations of chlorine in the presence of zinc. From a series of experiments previously made I have determined that zinc does not interfere in this operation. The results of these experiments are as follows :

Solution.	No zinc.	Containing zinc.	Gram.
1	0.4883	0.4897	0.1
	0.4893	0.4901	0.2
2	0.4701	0.4895	0.5
	0.4900	0.4900	0.2
	0.4896 AgCl	0.4898 AgCl	

It is seen that the average of the four results obtained with 50 cc. portions of a hydrochloric acid solution containing no zinc differ by an insignificant quantity from those containing from one-tenth to five-tenths gram of zinc.

The remainder of the mixture of solution and precipitate, after the "Totals" had been drawn off, was thrown upon a dry filter, received into a dry flask and labeled "Filtrate." Upon this duplicate determinations of chlorine were made, 50 cc. being used for each. For results see Series IV., Experiment 22. They show plainly that chlorine is not present in the precipitate when two molecules of potassium hydroxide are present.

Using the same quantity of zinc chloride as above, I proceeded to add one and one-half, one, and one-half molecules of potassium hydroxide, and to note the change, if any, in the composition of the precipitate. The method of procedure was identical with that just described for two molecules, with the addition that duplicate determinations of zinc oxide present in the "Filtrates" were made in every case. The composition of the precipitate will be seen by reference to Series IV. It will be observed that no chlorine is carried down when two molecules of potassium hydroxide are used. On the other hand, with one and one-half molecules, 7.4 per cent. of the total chlorine is present in the precipitate, and the quantity decreases as the proportion of the potassium hydroxide decreases. Two experiments were made with five and eight molecules, points at which zinc hydroxide was redissolved. For results see Experiments 26 and 27. In neither case is any chlorine carried down, although with five molecules about the same quantity of zinc hydroxide is present in the solution as was found with one and one-half molecules, the point at which the maximum quantity of chlorine appeared in the precipitate.

Series IV.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.		Cl in filtrate.		Cl in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.
22	2	.0798	.0000	.0798	.0700 .0701	.0701	.0699 .0698	.0699	.0000	100.00	.00
23	1½	.0798	.0142	.0656	.0703 .0701	.0702	.0650 .0649	.0650	.0052	82.2	7.4
24	1	.0798	.0366	.0432	.0705 .0704	.0705	.0659 .0659	.0659	.0045	54.1	6.4
25	½	.0798	.0562	.0236	.0701	.0701	.0676 .0676	.0676	.0025	29.6	3.6
26	5	.0798	.0148	.0650	.0706 .0704	.0705	.0704 .0702	.0703	.0000	82.4	.00
27	8	.0798	.0323	.0475	.0702	.0702	.0699 .0701	.0700	.0000	60.2	.00

Series V.

The purpose of this series was to determine the action of zinc hydroxide upon potassium sulphate and potassium chloride in a system constituted according to the following equation:

$$ZnCl_2 + 2KOH + xK_2SO_4 = Zn(OH)_2 + 2KCl + xK_2SO_4.$$

I made up a solution as follows: Into a liter flask I introduced 100 cc. of zinc chloride solution, together with the same quantity of potassium sulphate as was used in Series I. and III.; then potassium hydroxide in the proportion of two molecules, and enough more to neutralize the free acid in the zinc chloride solution. The system was then made up to 1000 cc. (18½° C.) with water, and four portions of 50 cc. each were drawn off. In two of these, after dissolving the precipitate with nitric acid, I determined the total chlorine in the system. In the remaining two I dissolved the precipitate with hydrochloric acid and determined the total sulphur trioxide present. That the presence of zinc does not interfere with the accurate determination of sulphur trioxide as barium sulphate under these circumstances is seen from the constancy of the "Totals" in this series, as well as in their close agreement with all previous "Totals." The remaining solution and precipitate were then thrown upon a dry filter, and in the "Filtrate" duplicate determinations of chlorine and sulphur trioxide were made. For results see Experiments 28 and 29. No chlorine or sulphur trioxide appears in the precipitate with two molecules.

Using the same quantity of zinc chloride and potassium sulphate, and following the same methods as just described, I determined the composition of the precipitate with one and one-half molecules. Again, as referred to in the case of ferric hydroxide, Series III., it is seen that more zinc oxide appears in the precipitate under these circumstances than at the corresponding points in Series IV., when potassium sulphate was not present in the system. The same explanation serves here as was offered in the case of ferric hydroxide. With one and one-half molecules no chlorine appears in the precipitate, but 12 per cent. of the total sulphur trioxide is carried down.

Series V.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.		Cl in filtrate.		Cl in precipitate.	SO_3 in total.		SO_3 in filtrate.		SO_3 in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.	Per cent. total SO_3 in precipitate.
28	2	.0798	.0000	.0798	.0705 .0705	.0705	.0705 .0706	.0706	.0000	.1158 .1157	.1158	.1143 .1142	.1143	.0000	100.00	.00	.00
29	2	.0798	.0000	.0798		....		....	....	.1159 .1157	.1158	.1154 .1153	.1154	.0000	100.00	..	.00
30	1½	.0798	.0054	.0744	.0703 .0703	.0703	.0701 .0701	.0701	.0000	.1159 .1157	.1158	.1021 .1018	.1020	.0138	93.2	.00	12.0

Discussion.

The argument set forth in the discussion on ferric hydroxide holds good in the case of zinc hydroxide. In no case have chlorine or sulphur trioxide and potassium appeared in the precipitate at the same time ; again, neither have chlorine and sulphur trioxide appeared in the precipitate at the same time. The maximun quantity of acid, however, has uniformly appeared at a point short of two molecules where the quantity of zinc hydroxide is very little less than at complete precipitation. Here again, as in the previous discussion, we are justified in claiming for zinc hydroxide the power of decomposing substances. Further, the power of selective combination is conclusively shown in Series V., where sulphur trioxide is carried down in preference to chlorine.

Effect of Concentration.

Series VI.

It is well known that concentration plays an important part in reactions such as have been the subject of the foregoing discussion. To learn the magnitude of the disturbance brought about by concentration, I made the following experiments : I introduced 150 cc. of the zinc chloride solution into a 500 cc. flask, added potassium hydroxide in the proportion of two molecules, and proceeded to determine the chlorine in the "Totals" and "Filtrates" as in the previous work. It will be seen that all conditions here are the same as at the corresponding points in Series IV., except that the quantity of zinc chloride and potassium hydroxide in unit volume is multiplied by three. A similar experiment was also made, using one and one-half molecules. The results show a slight quantity of chlorine carried down in the case of two molecules (1.2 per cent. of the total), in this respect differing from those of the more dilute solutions in Series IV.

When one and one-half molecules are used, it is seen that the percentage of the total zinc oxide in the precipitate has decreased from 82.2 in the dilute solution in Series IV., to 81.5, and the chlorine in the precipitate has increased from 7.4 to

10.4 per cent. of the total present. Hence the tendency of concentration, so far as indicated, is to decrease the quantity of zinc oxide precipitated and to increase the quantity of chlorine carried down. In this series I examined qualitatively the basic "Filtrate" in the case of one and one-half molecules. Potassium sulphate and sodium sulphate produced a precipitate of zinc hydroxide. Acids and salts, however, other than those mentioned, produced no effect.

In addition to these experiments on zinc, two were made on iron with the same object in view. In this case again, the quantity of ferric chloride and potassium hydroxide was multiplied by three, and made up to 500 cc. "Totals" and "Filtrates" were made at corresponding points in Series II. With six molecules no chlorine appears in the precipitate. With five molecules, however, a change is noted. In the dilute solution, Experiments 16 and 17, 76.1 per cent. of the ferric oxide, and 4.5 per cent. of the chlorine were carried into precipitation. Under these conditions, however, 57.3 per cent. of the ferric oxide and 3.4 per cent. of the chlorine appear in the precipitate. In the case of iron, the tendency then of concentration is to decrease both the quantity of ferric oxide in the precipitate and the quantity of chlorine carried down. The basic solution of iron at this point gave some very interesting reactions. It was noted that upon standing the slight turbidity which often forms in a very basic solution immediately after filtration, cleared up and the solution took on a very dark red color. On the addition of a few drops of concentrated hydrochloric acid, a decided precipitate of ferric hydroxide was formed; with dilute hydrochloric acid the same; sulphuric acid, both dilute and strong, and any sulphate, cause a precipitate. Nitric acid, and nitrates other than those forming insoluble chlorides, gave no precipitate whatever; and further, sodium phosphate instead of giving ferric phosphate, produced a precipitation of all the iron in the solution in the form of ferric hydroxide.

Up to this point nothing has been said concerning potassium. In Series I. it was shown that, short of six molecules, no potassium appeared in the precipitate, but at and beyond that point potassium was carried down in very small quanti-

Series VI.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.	Cl in filtrate.	Cl in precipitate.	K_2O in total.	K_2O in filtrate.	K_2O in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.	Per cent. total K_2O in precipitate.
					.2095	.2073							
31	2	.2394	.0000	.2394	.2096	.2072	.0024	.2786	.2791	0	100.00	1.1	.00
					.2097	.2071						1.1	
					.2093	.2070							
32	2	.2394	.0000	.2394	.2093	.2070	.0023	....	....	..	100.00	1.1	
					.2093	.2070							
					.2096	.1876							
33	1½	.2394	.0344	.2050	.2096	.1876	.0220	....	....	..	81.5	10.4	..
					.2096	.1876							
		Fe_2O_3.	Fe_2O_3.	Fe_2O_3.									
					.3376	.3390			.4512				
34	6	.2400	.0000	.2400	.3379	.3389	.0000	.4532	.4528	0	100.00	.00	.00
					.3382	.3388			.4543				
					.3376	.3262							
35	5	.2400	.1112	.1288	.3377	.3262	.0115	.3773	.3835	0	53.7	3.4	.00
					.3378	.3262							

ties. In the last series just discussed, I made determinations of potassium in the solutions made up of ferric chloride with five and six molecules of potassium hydroxide. With the systems containing zinc chloride, however, I was unable to obtain satisfactory results, except with two molecules of potassium hydroxide. In none of these experiments was potassium found in the precipitate.

Effect of Temperature.

Series VII.

The object of this series of experiments was to determine the effect of temperature upon the phenomenon in question. I made one experiment with zinc, using one and one-half molecules of potassium hydroxide, and another with iron, using five molecules. The solutions in both cases were constituted as at corresponding points in Series IV. and Series II. respectively. The method of procedure was also the same with this exception: I divided the solution when made up into portions of 300 cc. and 200 cc., shaking thoroughly before dividing, so that the precipitate should be evenly distributed throughout the solution. From the 300 cc. portion I drew off two portions of 50 cc. each for "Totals." The remainder was filtered through a dry filter, and two portions of 50 cc. each used for the determination of chlorine in the "Filtrate." Also one portion of 50 cc. was used to determine the quantity of zinc hydroxide or ferric hydroxide, as the case might be, left in the filtrate. These determinations in "Totals" and "Filtrates" served as a check on the solution. The 200 cc. portion was boiled vigorously for five minutes in a 500 cc. flask, the mouth of which was covered with a watch crystal to prevent the escape of steam. The solution was next filtered, while hot, through a dry filter. Of this I used two portions of 50 cc. each for determinations of chlorine in the "Filtrate." Another portion of 50 cc. was used to determine the quantity of zinc hydroxide or ferric hydroxide, as the case may be, left in the "Filtrate."

The result of these experiments, as shown in Series VII., in the case of zinc, the total quantity of zinc oxide in precipita-

Series VII.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.	Cl in filtrate.	Cl in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.
36^1	1½	.0798	.0136	.0662	.0707 .0706 .0705	.0642 .0642 .0642	.0064	82.9	9.00
36^2	1½	.0798	.0240	.0558	....	.0692 .0692 .0692	.0014	69.9	1.9
		Fe_2O_3.	Fe_2O_3.	Fe_2O_3.				Fe_2O_3.	
37^1	5	.0800	.0250	.0550	.1127 .1126 .1125	.1073 .1074 .1074	.0053	68.8	4.7
37^2	5	.0800	.0316	.0484	....	.1111 .1110 .1109	.0016	60.5	1.4

[1] Not boiled.

[2] Boiled.

tion is reduced from 82.9 to 69.9 per cent. by boiling, and the total chlorine in the precipitate is reduced from 9.0 to 1.9 per cent.

Upon iron the general effect of boiling is the same as in the case of zinc. The total quantity of ferric oxide is reduced by boiling from 68.8 to 60.5 per cent., and the total chlorine in the precipitate is reduced from 4.7 to 1.4 per cent. The general conclusion then to be drawn from this series is that rise in temperature greatly reduces both the total metallic oxide and chlorine in the precipitate.

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REVIEWS.

THE PHASE RULE. By WILDER D. BANCROFT. The Journal of Physical Chemistry: Ithaca, New York. 1897.

Perhaps this book can be most fairly noticed by reprinting the author's preface. This course is accordingly followed: "There has been so much work done in physical chemistry during the last ten years that the mass of accumulated material is now too large to be remembered as miscellaneous facts. It becomes comparatively easy to survey the whole field if we consider the phenomena as examples illustrating a few general principles. Natural divisions of the subject are qualitative equilibrium, quantitative equilibrium, electrochemistry, and mathematical theory. The last two divisions are already recognized as sound; but the qualitative and quantitative phenomena have always been treated together, and the distinction between them has nowhere been clearly defined. My idea is that all qualitative experimental data should be presented as particular applications of the phase rule and the theorem of LeChatelier, while the guiding principles for the classification of quantitative phenomena should be the mass law and the theorem of Van 't Hoff."

"In this book I have tried to present the subject of qualitative equilibrium from the point of view of the phase rule and of the theorem of LeChatelier, without the use of mathematics. That such a treatment should be possible is due very largely to the work of H. W. Bakhuis Roozeboom, who has done far more than any one else to show the importance and significance of Gibbs's phase rule." E.

A TABULAR ATLAS OF THE CHEMISTRY OF THE METALS, comprising the arrangement on a novel plan in sectional and tabular form, devised to rapidly convey the information, of the data relating to the history, distribution, preparation, or metallurgy, properties, chemical, medical, pharmacal and technical uses, analysis and toxicology of the said metals, their organic and inorganic compounds.—METALS OF THE ALKALIES, CÆSIUM, RUBIDIUM AND POTASSIUM. BY JOHN FREMONT SLEEPER. Copyright, 1896, by the author.

Attention is here called to the beginning of an important undertaking, the preparation of a work of reference in the form of a large atlas, the subject of which is The Chemistry of the Metals. The author has been engaged upon the work for a number of years, and has his first volume now ready for publication. Publishers are, however, wary, and the author asks for subscribers, to come to his aid, $10 being the price of the volume.

There can be no doubt as to the desirability of such a work if well done. Everything depends upon its accuracy and thoroughness. Of these qualities it is impossible to judge in the case of Mr. Sleeper's Atlas, as only a few specimen pages are yet available in printed form. The general impression made by these pages is favorable, and it is to be hoped that the number of subscribers necessary to secure publication will soon be found. The amount of labor involved in the preparation of such an atlas is enormous, but this the author cheerfully faces. In a preliminary notice, after speaking of the impossibility of reaching perfection, he says: "Nevertheless, I lay this work before the public with the assurance that all has been done to render it perfect; that the most anxious care exercised by me, whose heart and soul are in the task, and who regards it as the allotted labor of his life, could effect, and that *three revisions* have been given to the more important matter it includes."

Perhaps the work is best described by calling it a somewhat mechanically-arranged, inorganic Beilstein. I. R.

NOTES ON ASSAYING. By PIERRE DE PEYSTER RICKETTS, E.M., Ph.D., and EDMUND H. MILLER, A.M., Ph.D. New York: John Wiley & Sons. 311 pp. 1897.

This is not a reprint of Prof. Ricketts' well-known *Notes on Assaying*, but is a book so much enlarged and improved that it is practically new. About one-half of the book treats of fire assays, giving the thorough and detailed instructions for which Professor Ricketts' old manual was noted. The rest of the book gives schemes of analyses of ores, laboratory tests, blowpipe analysis, and closes with a selection of tables useful to assayers. The best volumetric and electrolytic methods are given in the schemes of analysis. The book is brought up to date and will be welcomed as a worthy successor of the author's older manual. E. R.

A DETAILED COURSE OF QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES WITH EXPLANATORY NOTES. By ARTHUR A. NOYES, Ph.D., Assistant Professor of Chemistry in the Massachusetts Institute of Technology. Third revised and enlarged edition. New York: Macmillan Co. 1897. 88 pp. $1.25.

The number of analytic manuals in print leads to the belief that every teacher finds it necessary to write one for his students, and to publish it for the benefit of the public at large. If each new manual were as much better than its forerunners as is that of Professor Noyes, we might hope for the speedy appearance of the ideal final manual, the last word on the subject. The author begins by letting the student mix solutions of the salts of each group in order, separating the metals. Solutions of acids are similarly studied; then dry reactions. Now the student is ready for the analysis of unknown substances. Explicit directions for analysis are given, and copious notes explain every step. All preliminary "reaction" work is omitted from this book. In his preface the author defends this omission, denies the value to the average student of a more extended acquaintance with metathetical test-tube reactions, and would substitute, time permitting, a course in inorganic preparations. To those teachers intending to write new analytic manuals, examination of this book and careful study of the preface is recommended. E. RENOUF.

JAHRBUCH DER ELEKTROCHEMIE. BERICHTE ÜBER DIE FORTSCHRITTE DES JAHRES 1896. Unter Mitwirkung der Herren Prof. Dr. K. ELBS, Giessen, Prof. Dr. F. W. KUESTER, Göttingen. Im wissenschaftlichen Theile bearbeitet von Dr. W. NERNST, o. Professor an der Universität Göttingen. Im technischen Theile bearbeitet von Dr. W. BORSCHERS, Lehrer an der Kgl. Maschinenbau- und Hüttenschule zu Duisburg. III Jahrgang. Wilhelm Knapp: Halle, A. S. 1897. pp. 347.

The size of this volume, which reviews but the work of a year, serves to call attention to the importance which electrochemistry has acquired. The scientific portion of the book fills 72 pages. The remainder of the work is devoted to the technical side. One of the most interesting developments in electrochemistry during the past year or two is in connection with the dissociating action of different solvents. J. J. Thomson first pointed out a relation between the ionizing power of solvents and their dielectric constants, and Nernst, a little later, called attention to the same relation. The recent experimental work along this line has served to make probable the conclusion of Thomson and Nernst, which gives us for the first time an insight into the physical nature or *modus operandi* of electrolytic dissociation. Other chapters of special scientific interest are on "The Theory of the Origin of the Galvanic Current," "Polarization and Electrolysis," and "Dielectric Measurements."

A misstatement of fact, for which Nernst is responsible, occurs on page 5, in connection with my error in the conductivity of solutions of acetylene in water. It is stated that G. Bredig and A. Usoff showed that the conductivity of aqueous solutions of acetylene was extremely small, and on account of impurities could scarcely be determined—"Was H. C. Jones bald darauf bestätigte, indem er die Irrthümlichkeit seiner Messungen zugab." The fact is that I corrected the error in this JOURNAL, July, 1896, and the article by Bredig and Usoff did not appear in the *Zeitschrift für Elektrochemie* until September, 1896. It is a matter of small consequence, yet perhaps it is just as well that the facts should stand on record in their true relations. The chapter on electro-analysis was written by Prof. Küster.

Some of the more interesting advances in applied electrochemistry have been in connection with the transformation of chemical energy into electrical, including the methods of obtaining electricity directly from carbon. A large number of improvements have been made also in connection with the electrolytic deposition of the metals. The organic chemist will find the chapters on the electrolysis of organic compounds, and electrolytic reductions and oxidations, written by Prof. Elbs, both instructive and suggestive. The book as a whole gives a clear and concise résumé of the advances in the many fields which are touched by electrochemistry for the year which it represents, and this is almost a necessity in the case of electrochemistry, since the literature on this subject is so scattered that it is difficult to have access to every article when it first appears.

H. C. J.

GRUNDZÜGE DER ELEKTROCHEMIE von Dr. WALTHER LÖB, Privatdocent an der techn. Hochschule zu Aachen. Mit 43 in den Text gedruckten Abbildungen. J. J. Weber, Leipzig. 1887. pp. 140.

The subject of electrochemistry is rapidly becoming enriched by a number of text-books. Those deserving especial mention are, first, that portion of Ostwald's Lehrbuch devoted to this subject, then the works of Jahn, Le Blanc, and Lüpke, all of which treat the material at hand from a somewhat different standpoint.

This brief work which the author terms a catechism of electrochemistry, deals with the subject mainly from the scientific side. The last third of the work is, however, devoted to such matters as the forms of apparatus for obtaining the current, quantitative analysis by electrolysis with description of apparatus used, electrosynthesis, etc.

The arrangement of the subject-matter is, in places, apparently not entirely in keeping with the logical method. The theory of solutions is treated before the conductivity method, which has furnished much of the evidence on which the theory rests. The law of Faraday, which is fundamental to the whole subject, is not taken up until page 112 is reached, and is then discussed rather briefly. The book is not entirely free from errors, but in general is a concise statement of some of the more important facts connected with electrochemistry.

H. C. J.

TRAITÉ ÉLÉMENTAIRE DE MÉCANIQUE CHIMIQUE FONDÉE SUR LA THERMODYNAMIQUE. Par P. DUHEM, professeur de physique théorique a la faculté des sciences de Bordeaux. Tome II. Vaporisation et modifications analogues, continuité entre l'etat liquide et l'etat gazeux, dissociation des gas parfaits. Librairie Scientifique, A. Hermann. Paris, 1898. pp. 378.

The appearance of the first volume of this work has been recently noticed in this Journal.[1] It was divided into books one and two. The second volume comprises books three, four, and five. Book three, on *Vaporization*, treats of saturated vapors, the theory of boiling, fusion and allotropic modifications, dissociation, and vaporization of a substance in two different states.

Book four on the *Continuity of the Liquid and Gaseous States*, deals with the critical point, the principle of Thomson and Maxwell's theorem, the equation of the compressibility of fluids, the specific heat of fluids, and adiabatic transformations of saturated vapors. Book five, *Dissociation in Systems which contain a Mixture of Perfect Gases*, discusses the laws of specific heat and specific volume of perfect gases, mixtures of perfect gases, dissociation in homogeneous gaseous systems, density of a dissociable gaseous combination, specific heat of such a combination, dissociation of ammonium carbamate and analogous compounds, and the dissociation of hydrogen selenide and analogous substances.

This work by M. Duhem is unquestionably the most systematic and comprehensive treatise on chemical mechanics from the mathematical standpoint, which has thus far appeared.

H. C. J.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER. von Dr. CH. M. VAN DEVENTER. Mit einem Vorwort von Prof. Dr. J. H. VAN'T HOFF. S. L. van Lovy, Amsterdam. Wilhelm Englemann, Leipzig. 1897. 167 pp.

The author states in his preface that he has endeavored to bring together the most important results in physical chemistry in such a way that this important branch of the new chemistry should be accessible to those who have not entered deeply into physics and mathematics.

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[1] This JOURNAL, 19, 621.

The first chapter deals with such fundamental definitions as that of matter, element, etc. The second has to do with the laws of chemical combination, especially of definite and multiple proportions. In the third the laws of gases are taken up, together with a brief discussion of atoms and molecules, the constitution of molecules, and the stereochemical theories of van't Hoff and Le Bel. The fourth chapter is devoted to thermochemistry and chemical equilibrium. The principle of maximum work, which undoubtedly contains much that is true, is discussed at considerable length, and then a number of its limitations are pointed out. The fifth, sixth, and seventh chapters treat, respectively, of solutions, photochemistry and the periodic system.

The most striking omission is that of electrochemistry. This subject is barely touched upon in the chapter on solutions, under electrolytic dissociation. This is certainly not a slight omission, since no one side of physical chemistry is more interesting or important than that treated under the broad subject of electrochemistry.

The book is clearly written and comes highly recommended by van't Hoff. H. C. J.

KALENDER FÜR ELEKTROCHEMIKER SOWIE TECHNISCHE CHEMIKER UND PHYSIKER. Für das Jahr 1897. Herausgegeben von Dr. A. NEUBERGER, Redakteur der "Elektrochemischen Zeitschrift." Mit einer Beilage. Fischer's technologischer Verlag, M. Krayn. Berlin. pp. 702.

The author states that, in the preparation of this Calendar, he has had in mind especially the subject of electrochemistry. Not only the electrochemist, however, but the chemist and physicist will find this to be a useful handbook. The data compiled in these tables are of both scientific and technical value, but rather more stress seems to have been laid upon the technical side than is usually done in such work.

One can find here information in regard to the specific gravity of substances alone and in solution, the solubility of substances under varying conditions, the resistance of solids and solutions to the passage of the current; and of a more practical character under the headings, machines, combustible materials, electrochemical and electrothermal methods of producing the current, quantitative chemical electrolysis, galvano-plastic, etc.

The amount of sheer drudgery required to prepare such a work as this is easily underestimated, and it is to be hoped that this book will prove of service in many directions.

H .C. J.

TRAITÉ ELEMENTAIRE DE CHIMIE. Chimie minerale et Chimie organique. Par A. Haller et P. T. Muller. Carré et Naud. Paris, 1896.

This treatise, which is divided into two parts, the one inorganic and the other organic, is intended for the use of students working for certificates of proficiency in the natural sciences, or for candidates for scientific degrees. These books are intended for text-books alone and contain no laboratory experiments. The part devoted to general chemistry is very clear and contains a large amount of information in a compact form. There are two features of the book to which, however, objection may well be made. Before taking up the study of the simplest element the student must learn the laws of combination, laws governing combination of gases, the different methods of determining molecular and atomic weights, the meaning of valence and principles of crystallography ; while only one page in the book is devoted to a discussion of the periodic system, and that the last one in the book. The classification throughout, even among the non-metals, is based on this system ; but the relationship between the different families and elements and the important generalizations which can be drawn from a study of this arrangement of the elements is not clearly brought out or emphasized. A method of qualitative analysis is also included in this volume. The paraffins and their derivatives are treated very thoroughly in the part devoted to organic chemistry; but the attempt is made to cover the whole field and, instead of treating benzene as a type of the aromatic series, and its derivatives in a thorough manner and pointing out the relations of the more complex compounds to it, mention is made of a large number of substances and their structural formulas given without the reasons for writing them so.

J. E. G.

Correction.

Professor Peckham has called my attention to an error in my paper on California petroleum in the last number of this Journal. The oil wells in the section near Ventura, as he informs me are from five hundred to two thousand feet deep.

CHARLES F. MABERY.